Bonding Energetics in Alkaline Metal Alkoxides and Phenoxides

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Abstract: The bonding energetics in a variety of alkaline metal, alkoxides and phenoxides, MOR, was investigated based on the corresponding enthalpies of formation in the crystalline state determined by reaction-solution calorimetry. The results obtained at 298.15 K were as follows: $\Delta_f H_m^o$(MOR, cr)/kJ mol^{-1} = 382.7 ± 1.4 ($LiOC_6H_5$), 513.6 ± 2.5 ($NaO\text{-}nC_6H_{13}$), 326.4 ± 1.4 ($NaOC_6H_5$), 375.2 ± 3.4 ($KOCH_3$), 434.5 ± 2.7 (KOC_2H_5), 467.1 ± 5.2 ($KO\text{-}nC_3H_7$), 459.3 ± 2.1 ($KO\text{-}nC_4H_9$), 464.6 ± 5.7 ($KO\text{-}tC_4H_9$), 464.3 ± 2.5 ($KO\text{-}nC_6H_{13}$), 333.3 ± 3.1 (KOC_6H_5), 380.6 ± 2.9 ($RbOCH_3$), 434.1 ± 2.9 ($RbOC_2H_5$), 345.3 ± 2.9 ($LiOC_6H_5$), 379.1 ± 3.0 ($CsOCH_3$), 432.3 ± 3.1 ($CsOC_2H_5$), 466.9 ± 5.0 ($CsO\text{-}nC_3H_7$), 461.3 ± 3.5 ($CsO\text{-}nC_4H_9$), 461.9 ± 2.5 ($CsO\text{-}tC_4H_9$), 349.2 ± 1.4 ($CsOC_6H_5$). These results together with revised $\Delta_f H_m^o$(MOR, cr) values from the literature, were used to derive a consistent set of lattice energies for the MOR compounds and discuss general trends in the structure–energetics relationship based on the Kapustinskii equation.

Keywords: alkaline metals · enthalpy of formation · lattice energy · thermochemical radii · thermochemistry

Introduction

Alkaline metal alkoxides and phenoxides (MOR), are binary compounds where an alkaline metal M (M = Li, Na, K, Rb, Cs) binds to an alkoxy or phenoxy group (OR). They can be regarded as derivatives of the corresponding alcohols (ROH) in which the hydroxyl hydrogen has been replaced by an alkaline metal.[1–3] Alkaline metal alkoxides and phenoxides have considerable importance in synthetic chemistry, as strong bases or as nucleophilic agents.[1–4] They are also industrially relevant, for example, as additives to improve the temperature and pressure resistance of mineral lubricant oils and to minimise the corrosive properties of detergents.[1, 5] Most notably, sodium phenoxide is the starting material of the Kolbe–Schmitt process (i.e., carboxylation of $NaOC_6H_5$ by a stream of CO_2), which has been used on an industrial scale to produce salicylic acid since 1874.[6, 7]

Structural and energetic studies of alkaline metal alkoxides are scarce. X-ray diffraction information exists only for the methoxy, *tert*-butoxy, and phenoxy derivatives. These results indicate that the structures adopted in the solid state are critically dependent on the size of the metal and of the ligand. Lithium[8, 9] and sodium[8, 10] methoxides exhibit a two-dimensional layered polymeric structure, with each metal coordinated to four oxygen atoms, the M–O distances being d_{Li-O} = 195 pm[8, 9] and d_{Na-O} = 232 pm.[10] A different polymeric double layered structure is found for $KOCH_3$,[11, 12] $RbOCH_3$,[12] and $CsOCH_3$,[12] in which the metal coordination number (CN) is five and, on average, d_{K-O} = 273 pm,[11, 12] d_{Rb-O} = 284 pm,[12] and d_{Cs-O} = 304 pm.[12] The solid-state structure of $LiO\text{-}tC_4H_9$ is still unknown. Sodium *tert*-butoxide is composed of hexameric and nonameric $NaO\text{-}tC_4H_9$ units with CN(Na) = 3 and mean d_{Na-O} = 225 pm.[13, 14] The potassium, rubidium, and caesium *tert*-butoxides are isostructural forming tetrameric cubane $(MO\text{-}tC_4H_9)_4$ units.[15–18] In this case the coordination number of the metals is three and the average M–O distances are d_{K-O} = 261 pm,[17] d_{Rb-O} = 276 pm,[17] and d_{Cs-O} = 292 pm.[18] The phenoxides MOC_6H_5

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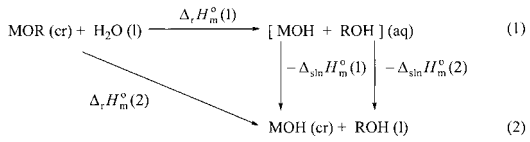
(M = Li, Na, K, Rb, Cs) adopt polymeric structures.[19, 20] In $NaOC_6H_5$, CN(Na) = 3 and, on average, $d_{Na-O} = 230.9$ pm.[19] In contrast, two different coordination spheres with metal coordination numbers of 3 and 6 are simultaneously observed in the isostructural KOC_6H_5,[20] $RbOC_6H_5$,[20] and $CsOC_6H_5$,[20] compounds. The average M–O bond lengths found, in these cases, are $d_{K-O} = 283$ pm,[20] $d_{Rb-O} = 296$ pm,[20] and $d_{Cs-O} = 317$ pm.[20]

Reports on the energetics of alkaline metal alkoxides are limited to a series of Li[21, 22] and Na[22, 23] compounds and to the ethoxides of K,[22] Rb,[24] and Cs.[24] These studies are extended in the present work to other Na, K, Rb and Cs derivatives. The use of the Kapustinskii equation[25] to estimate new enthalpy of formation data for MOR compounds is evaluated and general trends in the structure–energetics relationship are discussed.

Results and Discussion

The auxiliary enthalpy of formation and electroaffinity data used in the calculations are given in Table 1.[26–34] The molar quantities are based on the 2001 standard atomic masses.[35]

The enthalpies of formation of the metal alkoxides MOR (M = Li, R = C_6H_5; M = Na, R = nC_6H_{13}, C_6H_5; M = K, R = CH_3, C_2H_5, nC_3H_7, nC_4H_9, tC_4H_9, nC_6H_{13}, C_6H_5; M = Rb, R = CH_3, C_2H_5, C_6H_5; M = Cs, R = CH_3, C_2H_5, nC_3H_7, nC_4H_9, tC_4H_9, C_6H_5) investigated in this work, were obtained from calorimetric measurements of the enthalpies of reaction 1 and of the dissolution processes indicated in Equations (1) and (2). From those two Equations we can derive Equation (3).



$$\Delta_f H_m^\circ(\mathrm{MOR, cr}) = -\Delta_r H_m^\circ(1) + \Delta_{sln} H_m^\circ(1)\,\Delta_{sln} H_m^\circ(2) + \Delta_f H_m^\circ(\mathrm{MOH, cr}) + \Delta_f H_m^\circ(\mathrm{ROH, l/cr}) - \Delta_f H_m^\circ(\mathrm{H_2O, l}) \quad (3)$$

Here $\Delta_r H_m^\circ(1)$ represents the enthalpy change for the reaction of MOR with distilled and deionised water under the actual experimental conditions (see Experimental Section), $\Delta_{sln} H_m^\circ(1)$ is the enthalpy of dissolution of stoichiometric amounts of MOH in H_2O, and $\Delta_{sln} H_m^\circ(2)$ is the enthalpy of solution of ROH in aqueous MOH.

The concentrations of the MOH (M = Li, Na, K, Rb, Cs) compounds present in the final calorimetric solutions were always very small, with the typical molar ratios of $n_{MOH}:n_{H_2O}$ 1:6000 or less. The solutions were, therefore, assumed to be infinitely diluted and $\Delta_{sln} H_m^\circ(1)$ 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), -62.1 ± 1.1 kJ mol^{-1} (RbOH), and -71.0 ± 1.1 kJ mol^{-1} (CsOH), based on $\Delta_f H_m^\circ$(MOH, cr) and $\Delta_f H_m^\circ(\mathrm{MOH} \cdot \infty\, H_2O, \mathrm{aq})$ data reported in the literature.[26]

The fact that very diluted MOH solutions were formed in the calorimetric experiments also led us to assume that $\Delta_{sln} H_m^\circ(2)$ could be identified with the enthalpies of solution of the alcohols in pure water. This assumption had been previously found to be valid, since experimental measurements of the enthalpy of solution of *n*-butanol in water, and in diluted aqueous solutions of LiOH and NaOH, led to identical results within the experimental errors.[21, 23] The values of $\Delta_{sln} H_m^\circ(2) = -7.3 \pm 0.4$ kJ mol^{-1} (methanol), -10.7 ± 0.6 kJ mol^{-1} (ethanol), calculated from $\Delta_f H_m^\circ$(ROH, l) and $\Delta_f H_m^\circ(\mathrm{ROH} \cdot \infty\, H_2O, \mathrm{aq})$[26] data reported in the literature were selected. The values of $\Delta_{sln} H_m^\circ(2) = -7.75 \pm 0.39$ kJ mol^{-1} (*n*-butanol), -14.67 ± 0.54 kJ mol^{-1} (*tert*-butanol), and -16.38 ± 0.43 kJ mol^{-1} (phenol) were taken from ref. [23]. In the case of *n*-hexanol $\Delta_{sln} H_m^\circ(2) = -4.6 \pm 1.1$ kJ mol^{-1} was experimentally obtained in this work. For *n*-propanol $\Delta_{sln} H_m^\circ(2) = -9.2 \pm 1.0$ kJ mol^{-1} was estimated from a linear plot of the enthalpies of solution of ethanol, *n*-butanol, and *n*-hexanol quoted above against the number of carbon atoms in the alkyl chain. This plot has a regression coefficient of 0.9998.

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

Compound	$\Delta_f H_m^\circ$	Ref.	$\Delta_{ea} H_m^\circ$(OR)	Ref.
LiOH, cr	-484.93 ± 0.08	26		
NaOH, cr	-425.609 ± 0.008	26		
KOH, cr	-424.76 ± 0.08	26		
RbOH, cr	-418.19 ± 0.08	26		
CsOH, cr	-417.23 ± 0.08	26		
CH_3OH, l	-239.2 ± 0.2	27		
C_2H_5OH, l	-277.6 ± 0.3	27		
nC_3H_7OH, l	-302.6 ± 0.4	27		
nC_4H_9OH, l	-327.3 ± 0.4	27		
tC_4H_9OH, l	-359.2 ± 0.8	27		
$nC_6H_{13}OH$, l	-377.5 ± 0.5	27		
C_6H_5OH, cr	-165.1 ± 0.7	27		
H_2O, l	-285.830 ± 0.040	28		
OH, g	37.28 ± 0.29	29	182.3 ± 0.2	[34]
OCH_3, g	17.2 ± 3.8	30	157.7 ± 2.1	[34]
OC_2H_5, g	-15.5 ± 3.3	30	172.7 ± 3.2	[34]
O-nC_3H_7, g	-41.4 ± 4.2	31	178.8 ± 3.2	[34]
O-iC_3H_7, g	-52.3 ± 4.2	31	183.6 ± 2.8	[34]
O-nC_4H_9, g	-62.8 ± 4.2	31	177.9 ± 14.5	[34]
O-tC_4H_9, g	-90.8 ± 4.2	31	190.7 ± 5.2	[34]
O-nC_6H_{13}, g	-103.9 ± 5.0	32	189.5 ± 19.3	[34]
O-nC_8H_{17}, g	-143.6 ± 5.1	32	199.2 ± 19.3	[34]
OC_6H_5,g	56.9 ± 2.4	33	188.5 ± 0.2	[34]

The results of the experimental measurements of $\Delta_r H_m^\circ(1)$ (Table 2), $\Delta_{sln} H_m^\circ(1)$, and $\Delta_{sln} H_m^\circ(2)$, in conjunction with the auxiliary data in Table 1 enabled the calculation of $\Delta_f H_m^\circ$(MOR, cr) through Equation (3). The values obtained are compared in Table 2 with experimental data published earlier and also with estimates based on the Kapustinskii equation (see below). All experimental results reported in this work are the mean of at least four independent measurements and the uncertainties quoted represent twice the standard deviation of the mean.

Blanchard and co-workers[22] previously determined $\Delta_f H_m^\circ(LiOC_2H_5, cr) = -332.2 \pm 4.2$ kJ mol^{-1}, $\Delta_f H_m^\circ(NaOC_2H_5, cr) = -490.8 \pm 5.9$ kJ mol^{-1}, and $\Delta_f H_m^\circ(KOC_2H_5, cr) = -496.2 \pm 5.9$ kJ mol^{-1} from reaction of the $MOCH_3$ salts with H_2SO_4(aq). These values were subsequently changed without explanation to $\Delta_f H_m^\circ(LiOC_2H_5, cr) = -454.4 \pm 4.2$ kJ mol^{-1}, $\Delta_f H_m^\circ(NaOC_2H_5, cr) = -410.9 \pm 5.9$ kJ mol^{-1}, and $\Delta_f H_m^\circ(KOC_2H_5, cr) = -409.2 \pm 5.9$ kJ mol^{-1}, in a publication

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

MOR	$-\Delta_r H^\circ_m(1)$[a]	$-\Delta_f H^\circ_m$(MOR, cr) Experimental[b]	Estimated[c]	Δ[d]
LiOH		484.93 ± 0.08[e]	495.7	10.7
$LiOCH_3$		433.0 ± 2.4[f]	432.1	− 0.9
$LiOC_2H_5$		474.2 ± 2.1[f]	479.4	5.2
LiO-nC_3H_7			538.1	
LiO-iC_3H_7		499.3 ± 1.4[f]	502.9	3.6
LiO-nC_4H_9		512.33 ± 0.89[f]	510.8	− 1.5
LiO-tC_4H_9		508.6 ± 2.2[f]	502.7	− 5.9
LiO-nC_6H_{13}			607.2	
LiO-nC_8H_{17}			637.2	
$LiOC_6H_5$	21.43 ± 0.87	382.7 ± 1.4	366.6	− 16.1
NaOH		425.609 ± 0.008[e]	428.6	3.0
$NaOCH_3$		373.6 ± 1.9[g]	380.0	6.4
$NaOC_2H_5$		411.6 ± 1.9[g]	427.4	15.8
NaO-nC_3H_7			479.5	
NaO-iC_3H_7		461.6 ± 1.7[g]	456.8	− 4.7
NaO-nC_4H_9		463.9 ± 5.0[g]	464.0	0.1
NaO-tC_4H_9		477.1 ± 3.0[g]	467.5	− 9.6
NaO-nC_6H_{13}	52.8 ± 2.0	513.6 ± 2.5	491.8	− 21.8
NaO-nC_8H_{17}		526.3 ± 4.8[g]	526.3	0.0
$NaOC_6H_5$	39.38 ± 0.85	326.4 ± 1.4	334.8	8.4
KOH		424.764 ± 0.008[e]	409.5	− 15.3
$KOCH_3$	67.8 ± 3.3	375.2 ± 3.4	371.3	− 3.9
KOC_2H_5	50.3 ± 2.5	434.5 ± 2.7	418.8	− 15.7
KO-nC_3H_7	41.2 ± 5.0	467.1 ± 5.2	466.2	− 0.9
KO-iC_3H_7			452.4	
KO-nC_4H_9	72.3 ± 1.9	459.3 ± 2.1	459.0	− 0.3
KO-tC_4H_9	105.8 ± 5.6	464.6 ± 5.7	470.8	6.2
KO-nC_6H_{13}	114.3 ± 2.0	464.3 ± 2.5	492.4	28.1
KO-nC_8H_{17}			530.2	
KOC_6H_5	44.7 ± 2.9	333.3 ± 3.1	340.7	7.4
RbOH		418.19 ± 0.08[e]	417.7	− 0.5
$RbOCH_3$	60.4 ± 2.6	380.6 ± 2.9	380.9	0.3
$RbOC_2H_5$	48.7 ± 2.6	434.1 ± 2.9	428.4	− 5.7
RbO-nC_3H_7			475.1	
RbO-iC_3H_7			462.5	
RbO-nC_4H_9			469.0	
RbO-tC_4H_9			482.0	
RbO-nC_6H_{13}			503.2	
RbO-nC_8H_{17}			541.4	
$RbOC_6H_5$	30.6 ± 2.7	345.3 ± 2.9	352.2	6.9
CsOH		417.23 ± 0.08[e]	408.7	− 8.6
$CsOCH_3$	69.8 ± 2.8	379.1 ± 3.0	375.3	− 3.8
$CsOC_2H_5$	58.4 ± 2.8	432.3 ± 3.1	422.7	− 9.6
CsO-nC_3H_7	47.3 ± 4.8	466.9 ± 5.0	468.0	1.1
CsO-iC_3H_7			458.2	
CsO-nC_4H_9	76.2 ± 3.3	461.3 ± 3.5	464.6	3.3
CsO-tC_4H_9	114.4 ± 2.0	461.9 ± 2.5	480.2	18.4
CsO-nC_6H_{13}			500.6	
CsO-nC_8H_{17}			539.9	
$CsOC_6H_5$	34.72 ± 0.87	349.2 ± 1.4	351.3	2.1

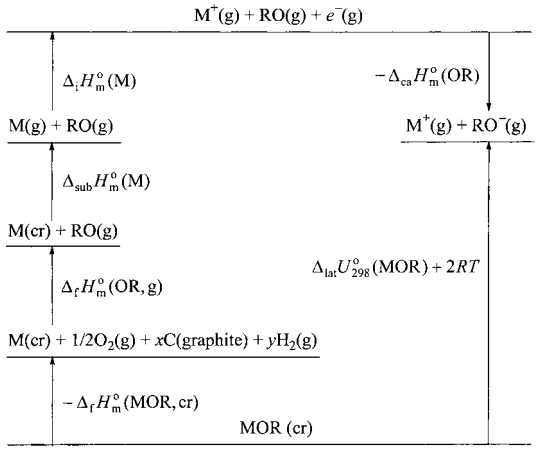
[a] This work, reaction with water (see text). [b] This work, unless otherwise stated (see text). [c] Estimated using Kapustinskii equation. [d] $\Delta = \Delta_f H^\circ_m$(exptl) − $\Delta_f H^\circ_m$(estd). [e] Ref. [26]. [f] Ref. [21]. [g] Ref. [23].

where $\Delta_f H^\circ_m(RbOC_2H_5, cr) = -403.8 \pm 4.2$ kJ mol^{-1}, and $\Delta_f H^\circ_m(CsOC_2H_5, cr) = -404.2 \pm 4.2$ kJ mol^{-1} were reported.[24] Except for $\Delta_f H^\circ_m(NaOC_2H_5, cr) = -410.9 \pm 5.9$ kJ mol^{-1} these results are considerably different from the corresponding values in Table 2. The origin of this discrepancy was, however, impossible to evaluate.[21] The enthalpy of formation of $NaOC_6H_5$ redetermined in this work (Table 2) is in very good agreement with $\Delta_f H^\circ_m(NaOC_6H_5, cr) = -326.2 \pm 3.7$ kJ mol^{-1} we previously reported.[23]

If an ionic structure is assumed for each MOR compound in the solid state, the corresponding lattice energy, $\Delta_{lat}U^\circ$(MOR), can be defined as the *internal energy* change associated with the following process:[25]

$$MOR(cr) \rightarrow M^+(g) + RO^-(g) \quad (4)$$

(M = alkaline metal; R = alkyl or phenyl). The value of $\Delta_{lat}U^\circ$(MOR) at 298.15 K, $\Delta_{lat}U^\circ_{298}$(MOR), can be computed from Equation (5) which directly results from the Born–Haber cycle in Scheme 1.



Scheme 1.

$$\Delta_{lat}U^\circ_{298}(MOR) = -\Delta_f H^\circ_m(MOR, cr) + \Delta_f H^\circ_m(OR, g) + \Delta_{sub}H^\circ_m(M) + \Delta_i H^\circ_m(M) - \Delta_{ea}H^\circ_m(OR) - 2RT \quad (5)$$

In this Equation R is the gas constant, T is the absolute temperature, $\Delta_{sub}H^\circ_m(M)$ and $\Delta_i H^\circ_m(M)$ represent the enthalpy of sublimation and the enthalpy of ionisation of the metal, respectively, and $\Delta_{ea}H^\circ_m$ is the enthalpic electron affinity of the OR radical. The obtained $\Delta_{lat}U^\circ_{298}$(MOR) values are compared in Table 3 and in Figure 1 with the lattice enthalpies previously reported by us for several LiOR and NaOR compounds,[21, 23] recalculated using more recent auxiliary data. These results were derived by using $\Delta_{sub}H^\circ_m(M) = 159.37 \pm 0.08$ kJ mol^{-1} (Li),[26] 107.32 ± 0.08 kJ mol^{-1} (Na),[26] 60.59 ± 0.08 kJ mol^{-1} (K),[26] 80.88 ± 0.08 kJ mol^{-1} (Rb),[26] 76.065 ± 0.008 kJ mol^{-1} (Cs);[26] $\Delta_i H^\circ_m(M) = 526.41 \pm 0.08$ kJ mol^{-1} (Li),[26] 502.04 ± 0.08 kJ mol^{-1} (Na),[26] 425.02 ± 0.08 kJ mol^{-1} (K),[26] 409.22 ± 0.08 kJ mol^{-1} (Rb),[26] 381.90 ± 0.08 kJ mol^{-1} (Cs);[26] 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 is observed in Table 3 and Figure 1. Most evident is, however, the considerable decrease of $\Delta_{lat}U^\circ_{298}$(MOR) with the increase of branching in the alkyl chain.

The lattice energy values obtained may be analysed using the Kapustinskii approximation represented by Equation (6),[25] 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.

Table 3. Lattice energies of the alkaline metal alkoxides (in kJ mol^{-1}) and thermochemical radii (in pm) of the metals and of the alkoxide and phenoxide anions.

M	OR	r_-	$\Delta_{lat}U^o_{298}$(MOR) Estimated[a]	Experimental[b]
Li	OH	123.5	1031.7	1021.0 ± 0.5
$r_+ = 85.6$	OCH_3	136.3	972.5	973.3 ± 5.0
	OC_2H_5	136.4	972.0	966.8 ± 5.1
	O-nC_3H_7	130.4	998.8	
	O-iC_3H_7	142.0	947.8	944.2 ± 5.2
	O-nC_4H_9	141.3	950.9	952.5 ± 15.1
	O-tC_4H_9	153.6	902.0	907.9 ± 7.0
	O-nC_6H_{13}	149.4	918.2	
	O-nC_8H_{17}	154.4	898.8	
	OC_6H_5	157.7	886.9	902.9 ± 2.8
Na	OH	123.5	888.2	885.2 ± 0.5
$r_+ = 119.4$	OCH_3	136.3	843.9	837.5 ± 4.7
	OC_2H_5	136.4	843.6	827.8 ± 5.0
	O-nC_3H_7	130.4	863.7	
	O-iC_3H_7	142.0	825.3	830.1 ± 5.3
	O-nC_4H_9	141.3	827.7	827.6 ± 15.9
	O-tC_4H_9	153.6	790.4	800.0 ± 7.3
	O-nC_6H_{13}	149.4	802.8	824.6 ± 20.1
	O-nC_8H_{17}	154.4	787.9	787.9 ± 20.5
	OC_6H_5	157.7	778.7	770.3 ± 2.8
K	OH	123.5	774.0	789.3 ± 0.5
$r_+ = 155.3$	OCH_3	136.3	740.1	744.0 ± 5.5
	OC_2H_5	136.4	739.9	755.6 ± 5.3
	O-nC_3H_7	130.4	755.2	756.2 ± 7.4
	O-iC_3H_7	142.0	725.8	
	O-nC_4H_9	141.3	727.6	727.9 ± 15.2
	O-tC_4H_9	153.6	698.6	692.4 ± 8.8
	O-nC_6H_{13}	149.4	708.3	680.2 ± 20.1
	O-nC_8H_{17}	154.4	696.7	
	OC_6H_5	157.7	689.5	682.1 ± 4.0
Rb	OH	123.5	758.0	758.5 ± 0.5
$r_+ = 161.2$	OCH_3	136.3	725.5	725.2 ± 5.2
	OC_2H_5	136.4	725.3	731.0 ± 5.4
	O-nC_3H_7	130.4	740.1	
	O-iC_3H_7	142.0	711.7	
	O-nC_4H_9	141.3	713.5	
	O-tC_4H_9	153.6	685.6	
	O-nC_6H_{13}	149.4	694.9	
	O-nC_8H_{17}	154.4	683.7	
	OC_6H_5	157.7	676.8	670.0 ± 3.8
Cs	OH	123.5	716.9	725.4 ± 0.5
$r_+ = 177.5$	OCH_3	136.3	687.8	691.6 ± 5.3
	OC_2H_5	136.4	687.5	697.1 ± 5.5
	O-nC_3H_7	130.4	700.8	699.7 ± 7.3
	O-iC_3H_7	142.0	675.4	
	O-nC_4H_9	141.3	676.9	673.6 ± 15.5
	O-tC_4H_9	153.6	651.8	633.4 ± 7.1
	O-nC_6H_{13}	149.4	660.2	
	O-nC_8H_{17}	154.4	650.1	
	OC_6H_5	157.7	643.8	641.7 ± 2.8

[a] Estimated from Equation (6) by using the r_+ and r_- values listed in this Table. [b] Experimental values calculated from Equation (5).

$$\Delta_{lat}U^o_0(\mathrm{MOR}) = 1.079 \times 10^5 \frac{\nu Z_+ Z_-}{r_+ + r_-} \quad (6)$$

In this expression, $\Delta_{lat}U^o_0$(MOR) is the lattice energy at 0 K in kJ mol^{-1}, ν is the number of ions in the molecule (in this case, $\nu = 2$), Z_+ and Z_- are the charges of the cation and the anion, respectively, and r_+ and r_- the corresponding radii in pm. Note that $\Delta_{lat}U^o_0$(MOR) is related with $\Delta_{lat}U^o_{298}$(MOR) in Table 3 through Equation (7).

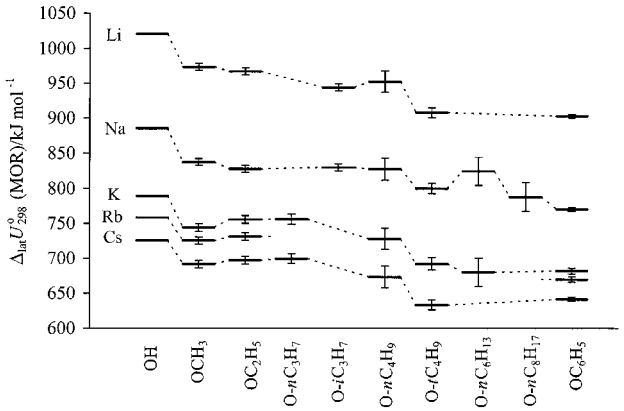


Figure 1. Lattice energies of alkaline metal alkoxides and phenoxides.

$$\Delta_{lat}U^o_{298}(\mathrm{MOR}) = \Delta_{lat}U^o_0(\mathrm{MOR}) + (H^o_{298} - H^o_0)_{M^+} + (H^o_{298} - H^o_0)_{OR^-} - (H^o_{298} - H^o_0)_{MOR} - 2RT \quad (7)$$

where R is the gas constant and $T = 298.15$ K. The information needed to compute the correction term $X = (H^o_{298} - H^o_0)_{M^+} + (H^o_{298} - H^o_0)_{OR^-} - (H^o_{298} - H^o_0)_{MOR} - 2RT$ is not available for the alkoxides 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. For example, in the case of the Li, Na, and K hydroxides, $X = 2.43$, -0.64, and -2.30 kJ mol^{-1}, respectively.[26] Hence, in the following discussion it will be assumed that, to a good approximation, $\Delta_{lat}U^o_{298}(\mathrm{MOR}) = \Delta_{lat}U^o_0$(MOR).

From Equation (6) and the experimental $\Delta_{lat}U^o_{298}$(MOR) data in Table 3 it was possible to derive the M−OR interatomic distances, $(r_+ + r_-)$. The individual r_+ and r_- values were subsequently obtained as follows. First the ionic radii of the cations given by Shannon,[36] $r_+(Li^+) = 90$ pm, $r_+(Na^+) = 116$ pm, $r_+(K^+) = 152$ pm, $r_+(Rb^+) = 166$ pm, and $r_+(Cs^+) = 181$ pm, were used to compute the radii of the alkoxide anions. For each anion, the mean of the r_- values obtained for different metals, was derived. This led to values of $r_-(OH) = 121$ pm, $r_-(OCH_3) = 135$ pm, $r_-(OC_2H_5) = 134$ pm, r_-(O-nC_3H_7) = 130 pm, r_-(O-iC_3H_7) = 141 pm, r_-(O-nC_4H_9) = 141 pm, r_-(O-tC_4H_9) = 155 pm, r_-(O-nC_6H_{13}) = 156 pm, r_-(O-nC_8H_{17}) = 158 pm and $r_-(OC_6H_5) = 164$ pm. These r_+ and r_- values were then selected as first approximations to obtain the final r_+ and r_- values (Table 3) by using the *solver* tool of MS Excel 7.0 to minimise the sum of the squares of the deviations between calculated and experimental $\Delta_{lat}U^o_{298}$(MOR). As shown in Figure 2 the sequence of experimental lattice energies in Table 3 is determined primarily by the interatomic distances $r_+ + r_-$.

Also presented in Table 3 are the lattice enthalpies of the alkaline metal alkoxides and phenoxides estimated from Equation (6) by using the appropriate r_+ and r_- data. It is concluded that Equation (6) reproduces the experimental $\Delta_{lat}U^o_{298}$(MOR) data with an average absolute deviation of 7.2 kJ mol^{-1} and a maximum relative deviation of 4.0%. The $\Delta_{lat}U^o_{298}$(MOR) values obtained were subsequently used to estimate the enthalpies of formation of various MOR com-

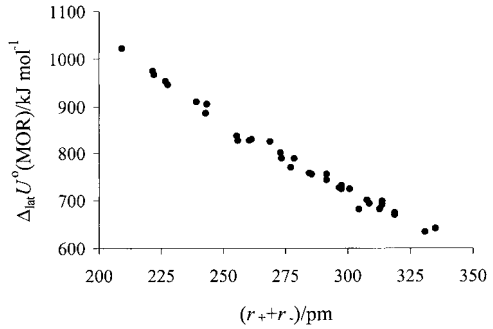


Figure 2. Lattice energies of alkaline metal alkoxides and phenoxides against the corresponding $r_+ + r_-$ derived from Equation (6).

pounds from Equation (5). As mentioned above, those results are listed in Table 2.

The r_+ and r_- calculated by the above procedure are called "thermochemical radii". Little absolute significance should be attached to them, as their principal value lies merely in their capacity to reproduce the lattice energies through Equation (6). This is shown, for example, by the fact that all interatomic $r_+ + r_-$ values calculated from the individual r_+ and r_- data in Table 3 for the methoxides are smaller than the corresponding values for the *tert*-butoxides, while the opposite conclusion is reached based on the experimental d_{M-O} interatomic distances previously mentioned in the Introduction. Note, however, that, as shown in Figure 3, excellent linear correlations are found by plotting d_{M-O} against $r_+ + r_-$. The lines in Figure 3 correspond to equations (d_{M-OCH_3}, $d_{M-tOC_4H_9}$, $d_{M-OC_6H_5}$, and $r_+ + r_-$ in pm):

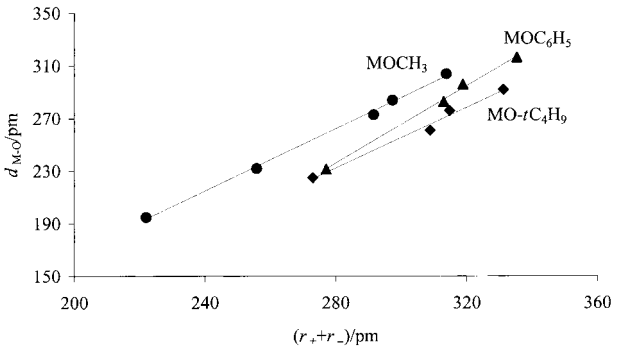


Figure 3. Experimental interatomic distances d_{M-O} against the corresponding $r_+ + r_-$ derived from Equation (6).

$$d_{M-OCH_3} = (1.182 \pm 0.033) \cdot (r_+ + r_-) - (68.87 \pm 9.11) \quad (8)$$

$$d_{M-tOC_4H_9} = (1.1604 \pm 0.099) \cdot (r_+ + r_-) - (92.70 \pm 30.55) \quad (9)$$

$$d_{M-OC_6H_5} = (1.4776 \pm 0.055) \cdot (r_+ + r_-) - (177.84 \pm 17.15) \quad (10)$$

with correlation coefficients of 0.998, 0.993 and, 0.999, respectively. Based on Equations (9) and (10) it is possible to predict that $d_{Li-O} = 185$ pm in $LiO\text{-}tC_4H_9$ and $d_{Li-O} = 182$ pm in $LiOC_6H_5$, respectively.

The lattice energies of the alkoxide compounds in Table 3 are rather high, only some 50–100 kJ mol^{-1} lower than the corresponding hydroxides, suggesting in principle a considerable ionic character for the M–OR bonds. The predominantly ionic character of the various alkoxides investigated in this work could also be suggested by the success of Kapustinskii equation in reproducing their enthalpies of formation (Table 2) and by the use of a diagram first proposed by Sproul for solid binary compounds[37, 38] (Figure 4). This two-dimensional graph has been shown to provide suggestive insights into the nature of bonding by separating ionic, metallic, and covalent compounds into three distinctly demarcated areas. In Figure 4 χ_{hi} and χ_{lo} are the highest and the lowest values of the

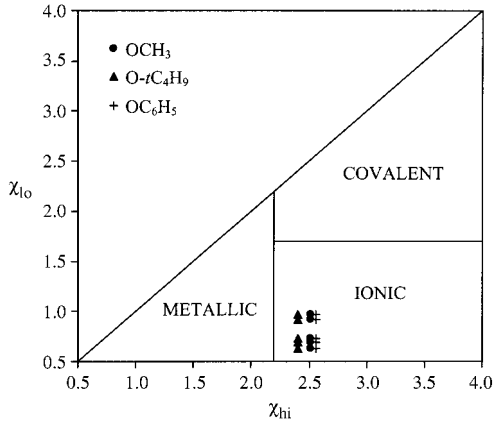


Figure 4. Ionic character of the alkaline metal alkoxides and phenoxides evaluated in terms of the highest (χ_{hi}) and lowest (χ_{lo}) values of the electronegativities of the species (atoms or groups of atoms) directly involved in bonding (see text).

electronegativities of the species (atoms or groups of atoms) directly involved in the bond of interest, respectively (e.g. M–OR in the case of the alkaline metal alkoxides or phenoxides). The vertical and horizontal limiting lines correspond to $\chi_{hi} = 2.2$ and $\chi_{lo} = 1.7$, respectively, as proposed by Sproul.[38] The plots for the methoxides, *tert*-butoxides and phenoxides indicated in Figure 4 were based on the following electronegativity data (Pauling's scale):[39, 40] $\chi(Li) = 0.97$, $\chi(Na) = 0.91$, $\chi(K) = 0.73$, $\chi(Rb) = 0.69$, $\chi(Cs) = 0.62$, $\chi(OCH_3) = 2.52$, $\chi(O\text{-}tC_4H_9) = 2.40$, and $\chi(OC_6H_5) = 2.56$. The group electronegativity of $O\text{-}tC_4H_9$ was calculated in this work by using the method proposed by Bratsch.[40] As shown in Figure 4 the data for the methoxides, *tert*-butoxides, and phenoxides, which are representative of MOR compounds with lattice enthalpies in the highest and lowest extremes of the range observed in Table 3, clearly fall in the ionic zone. Note, however, that the assignment of an ionic nature to these compounds does not in general agree with their structural and physical properties, whose main features can be associated with a predominance of covalency. As mentioned above the alkaline metal alkoxides and phenoxides are essentially polymeric or oligomeric. The degree of polymerisation varies with the nature of the metal and of the organic part of the molecule, notably decreasing with the increase of branching in the alkyl chain. The methoxides, for example, are involatile but show a polymeric structure in the solid state with a pronounced layer effect.[8–12] The tetrameric *tert*-butoxides of potassium, rubidium, and caesium sublime or dissolve in benzene, toluene and tetrahydrofuran (THF) without decomposition of the cubane $(MO\text{-}tC_4H_9)_4$ units existent in the solid state.[17, 41] Thus, as previously noted for other species,[42] the

ability to accurately predict enthalpies of formation of the alkaline metal alkoxides and phenoxides based on the ionic model and on a Born – Haber cycle such as that in Scheme 1 is not necessarily a sound reason to consider those compounds ionic in nature.

Experimental Section

General: All syntheses were carried out under an oxygen and water free (<5 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. Phenol (Merck, 99.8%) was sublimed twice. Methanol (Merck, 99.8%) and ethanol (Merck, 99.8%) were pre-dried over calcium sulfate, heated under reflux over activated magnesium and iodine, and finally distilled. All other alcohols (Merck, p.a.) were dried over calcium hydride and distilled. Potassium (Aldrich, 99.9%) was used as small pieces to which the oxidised surface was removed inside a glove-box. Rubidium and caesium (Aldrich, 99.95 + %) were kept inside a glove-box and used as supplied. Iodine was sublimed twice before use. All solvents were degassed twice by freeze-taw cycles before use.

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

Materials

Alkoxides: Sodium hexanoxide and all potassium alkoxides used in the calorimetric experiments were prepared by adding chunks of the metal to a solution containing the appropriate alcohol 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 white 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 rubidium and caesium alkoxides. In this case the metal was used in the form of small chips and added to an excess of the alcohol in THF solution. The IR spectra showed that the obtained alkoxides were alcohol and hydroxide free. Due to incomplete combustion it was impossible to obtain meaningful results from the elemental analysis of the compounds.

Lithium phenoxide: A 15% *tert*-butyllithium solution in *n*-pentane (Merck) was slowly added to a solution of phenol in THF, under vigorous magnetic stirring. The total time of addition/reaction was ca. 5 h. The excess phenol was extracted with pentane and the remaining solvent removed in vacuum. The obtained white solid was further dried in high vacuum (10^{-4} – 10^{-5} Torr), at room temperature, for two hours. The IR spectra showed the absence of phenol or hydroxide contamination. Elemental analysis calcd (%) for $LiOC_6H_5$ (100.05): C 72.03, H 5.00; found: C 70.80, H 5.50.

Sodium, potassium, rubidium, and caesium phenoxides: Phenol (Marca) was added during ca. 1 min to a stirred suspension of small pieces of the appropriate metal in THF. In the case of the sodium and potassium derivatives an excess of metal was used and the mixture was stirred for 1 – 2 h until hydrogen evolution stopped. The unreacted chunks of metal were removed and the remaining suspension taken to dryness. The obtained white solid was grinded, washed with pentane, and dried in vacuum at room temperature. The compound was further dried in high vacuum during 2 h. A similar method was followed in the preparation of the rubidium and caesium phenoxides, but in this case an excess of phenol was used. This excess of phenol was removed in vacuum. Typically the reaction duration was 4 h. The absence of phenol or hydroxide contamination was confirmed by IR spectroscopy. Elemental analysis calcd (%) for $NaOC_6H_5$ (116.10): C 62.07, H 4.33; found: C 61.09, H 4.83; for KOC_6H_5 (132.20): C 54.51, H 3.81; found: C 55.78, H 3.91; for $RbOC_6H_5$ (178.57): C 40.36, H 2.82; found: C 39.70, H 2.71; for $CsOC_6H_5$ (226.02): C 31.88, H 2.23; found: C 30.33, H 2.02.

Reaction-solution calorimetry: The enthalpies of reaction and solution needed to determine the enthalpies of formation of the alkaline metal alkoxides 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.[21] In brief, the calorimeter consisted of a transparent Dewar vessel closed by a lid, which supported 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 where the temperature was controlled at 298 ± 10^{-3} K by a Tronac PTC-40 unit. In typical experiment a thin walled glass ampoule was loaded with 20 – 100 mg of the alkoxide sample inside a glove box, sealed in vacuum, and weighed to $\pm 10^{-5}$ 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. 2.6 V was applied to a 48 Ω resistance during ca. 200 s. The enthalpy of solution of *n*-hexanol was measured by a similar procedure.

Acknowledgements

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