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Standard molar enthalpies of formation of lithium alkoxides

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Abstract

The standard ($p^0 = 0.1$ MPa) molar enthalpies of formation of several crystalline lithium alkoxides, ΔH_f^0(LiOR, cr), have been determined by reaction-solution calorimetry at 298.15 K. A linear correlation has been found between ΔH_f^0(LiOR, cr) and ΔH_f^0(ROH, l) for R = n-alkyl, enabling the prediction of data for other lithium alkoxides. The deviations from the linear correlation observed for R = ^{i}Pr and ^{t}Bu were tentatively explained in terms of the electronegativities of the OR groups. The experimental data were also used to derive the lattice energies and the thermochemical radii of the anions OR^-. The results were compared with those derived from the enthalpies of formation of the analogous sodium alkoxides, reported in a previous publication.

1. Introduction

Despite the wide use of alkaline metal alkoxides in chemical syntheses [1], their standard enthalpies of formation are usually not well established. In a previous publication [2] we reported the enthalpies of formation of several sodium alkoxides and we suggested that the values for many other alkaline metal alkoxides could be predicted from our results, with exception of those for the lithium compounds. The data for a number of these crystalline substances, obtained by reaction-solution calorimetry, are now presented and discussed. They rely on reactions (1) and (2), which proved to be fast, quantitative, and exothermic.

$$\mathrm{LiOR(cr)} + \mathrm{H_2O(l)} \longrightarrow \mathrm{LiOH(sln)} + \mathrm{ROH(sln)} \qquad (1)$$

$$\mathrm{LiOR(cr)} + \mathrm{HCl(aq)} \longrightarrow \mathrm{LiCl(sln)} + \mathrm{ROH(sln)} \qquad (2)$$

2. Experimental details

2.1. Materials

Methanol (Merck) and ethanol (Merck) were refluxed over activated magnesium and iodine and distilled. Isopropanol (Riedel de Haën), butanol (Merck), and t-butanol (Merck) were dried over calcium hydride and distilled. Lithium (Merck) was used as supplied.

2.2. Physical measurements

Infrared spectra were obtained with a Perkin–Elmer 577 spectrophotometer with samples mounted as Nujol mulls between KBr plates.

2.3. Lithium alkoxides syntheses

Lithium alkoxides are moisture sensitive. Therefore all syntheses and subsequent manipulations were conducted under dinitrogen. Alcohols were degassed before use. All syntheses were carried out in a similar way. Metallic lithium was added to an excess of alcohol and stirred for several h. The solution was then taken to dryness. The presence of water in the reaction media would lead to the formation of LiOH, very difficult to separate from the alkoxide. Small contaminations of LiOH may affect significantly the calorimetric results. Lithium alkoxides were characterized by IR

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spectroscopy, and neither alcohol nor LiOH was detected.

2.4. Calorimeter

The calorimeter used, built for the study of air- and moisture-hypersensitive compounds, and the experimental procedure were described in a previous paper [2]. The enthalpy change measured for the hydrolysis of TRIS (tris(hydroxymethyl)aminomethane) in a 0.1 M HCl aqueous solution, −29.89 ± 0.29 kJ/mol, agrees with the literature value for this test reaction [3]. All measurements were made at 298 K, and the results are averages of at least four runs. The errors presented are twice the standard deviation of the mean in each case.

3. Results and discussion *

Enthalpies of formation of lithium alkoxides can be calculated by using Scheme 1 and eqn. (3). Here, ΔH_r is the experimental enthalpy of reaction, ΔH_{d2} the enthalpy of solution of LiOH in water, and ΔH_{d3} the enthalpy of solution of the alcohol in H_2O + LiOH.

$$\begin{aligned}\Delta H_f^0(\text{LiOR, cr}) = {} & \Delta H_f^0(\text{LiOH, cr}) + \Delta H_f^0(\text{ROH, l}) \\ & - \Delta H_f^0(\text{H}_2\text{O, l}) \\ & - \Delta H_r + \Delta H_{d2} + \Delta H_{d3} \qquad (3)\end{aligned}$$

The concentrations of LiOH in solution were always very low (about 1 mol of LiOH to 1.5×10^4 mol of water). As this is close to infinite dilution, the value of the enthalpy of solution of LiOH in water (ΔH_{d2}) can be calculated as −23.55 kJ/mol, by using data in Table 1. Enthalpies of solution for the various alcohols, ΔH_{d3}, are presented in Table 2. The values for R = Me and Et were not measured but calculated as −7.3 ± 0.4 and −10.7 ± 0.6 kJ/mol, respectively, by using data in Table 1 and assuming that ΔH_{d3} are similar to the enthalpies of solution of MeOH and EtOH in water. This assumption is supported by the agreement between the results obtained for butanol in water and water + LiOH (Table 2). The negligible effect of the low concentration of lithium hydroxide on ΔH_{d3} was also observed in the case of sodium hydroxide [2], and accounts for the fact that the values for ^{i}PrOH and ^{t}BuOH shown in Table 2 were identified with the ones measured for the enthalpies of solution in water + NaOH [2]. The values for ΔH_r and the enthalpies of formation calculated from eqn. 3 are presented in Table 3.

TABLE 1. Supplementary thermochemical data

Compound	ΔH_f^0 (kJ/mol)	Reference
H_2O, l	−285.83	4a
CH_3OH, l	−239.1 ± 0.3	12
$CH_3OH:\infty H_2O$	−246.4 ± 0.3	12
C_2H_5OH, l	−277.5 ± 0.4	12
$C_2H_5OH:\infty H_2O$	−288.2 ± 0.4	12
i-C_3H_7OH, l	−318.1 ± 0.5	12
C_4H_9OH, l	−327.3 ± 0.4	12
t-C_4H_9OH, l	−359.2 ± 0.8	12
2-$C_5H_{11}OH$, l	−365.2 ± 1.1	12
$C_8H_{17}OH$, l	−426.5 ± 0.7	12
LiOH, cr	−484.93	4a
$LiOH:\infty H_2O$	−508.48	4a
LiCl, cr	−408.61	4a
HCl in $552H_2O$	−166.596	4a

As mentioned above, the thermochemical study of reaction 2 is an alternative method to obtain the enthalpies of formation of the alkoxides. This method was used in the case of LiOEt, to confirm the enthalpy of formation derived from eqn. (3). In Scheme 2 and eqn. (4) ΔH_r is the experimental enthalpy of reaction, ΔH_{d5} the enthalpy of solution of LiCl in the HCl aqueous solution, ΔH_{d6} the enthalpy of solution of ethanol in HCl aqueous solution + LiCl, and ΔH_{d7} the enthalpy of solution of water in 0.1 M HCl.

$$\begin{aligned}\Delta H_f^0(\text{LiOEt, cr}) = {} & \Delta H_f^0(\text{LiCl, cr}) + \Delta H_f^0(\text{EtOH, l}) \\ & - \Delta H_f^0(\text{HCl} \cdot 552\text{H}_2\text{O}) \\ & - \Delta H_r + \Delta H_{d5} + \Delta H_{d6} + 552 \Delta H_{d7} \qquad (4)\end{aligned}$$

ΔH_{d7} was found to be very close to zero ($552 \Delta H_{d7}$ less than *ca.* 2 kJ/mol). ΔH_{d5} was measured as −37.60 ± 0.52 kJ/mol and ΔH_{d6} as −7.79 ± 0.90 kJ/mol. The enthalpy of reaction and the derived enthalpy of formation of LiOEt are presented in Table 3.

The good agreement between the enthalpies of formation of lithium ethoxide derived from eqns. (3) and (4) (Table 3) supports the reliability of the remaining data obtained in the present study. It is noted, however, that our recommended value for ΔH_f^0(LiOEt, cr), −473.0 ± 2.5 kJ/mol (obtained from the reaction with water, Table 3), differs by about 17 kJ/mol from the value tabulated in NBS Tables [4a], −456.5 kJ/mol. This last value was probably based on the work by Blanchard *et al.*, who measured the enthalpy of hydrolysis of LiOEt in a 0.05 M sulphuric acid aqueous solution and recommended ΔH_f^0(LiOEt, cr) = −532.2 ± 4.2 kJ/mol [5]. The large discrepancy between our original result and the one given in NBS compilation is probably due to the fact that Blanchard *et al.* did not account for the dilution of the sulphuric acid in their calculation and/or made a calculation error.

Another issue that deserves comment regards a recent value for the standard enthalpy of formation of LiOH, ΔH_f^0(LiOH, cr) = −487.46 ± 0.10 kJ/mol [4b]. This differs from the value recommended in NBS Tables (Table 1) by −2.53 kJ/mol, a difference that

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* To accord with IUPAC recommendations, throughout this paper ΔH_f^0 should be read as $\Delta_f H_m^0$, ΔH_{sub}^0 as $\Delta_{cr}^{g} H_m^0$, and ΔH_{vap}^0 as $\Delta_l^g H_m^0$.

$$\begin{tikzcd}
\mathrm{LiOR(cr)} + \arrow[d, "\Delta H_r"] & \mathrm{H_2O(l)} \arrow[r, "\Delta H_r^0"] \arrow[d, "\Delta H_{d1}=0"] & \mathrm{LiOH(cr)} + \arrow[d, "\Delta H_{d2}"] & \mathrm{ROH(l)} \arrow[d, "\Delta H_{d3}"] \\
\{\mathrm{LiOH(sln)} + \mathrm{ROH(sln)} + (n-1)\mathrm{H_2O} & + \mathrm{H_2O}\} \arrow[r, "\Delta H=0"] & \{\mathrm{LiOH(sln)} + \mathrm{ROH(sln)} & + n\mathrm{H_2O}\}
\end{tikzcd}$$

Scheme 1.

TABLE 2. Enthalpies of solution of alcohols, ΔH_{d3}

Alcohol	ΔH_{d3} (kJ/mol)
CH_3OH	$-7.3\ \pm 0.4$ [a]
C_2H_5OH	$-10.7\ \pm 0.6$ [a]
$i\text{-}C_3H_7OH$	-13.18 ± 0.83 [b]
C_4H_9OH	-7.75 ± 0.39 [b]
	-7.92 ± 0.65 [c]
	-7.39 ± 0.59 [d]
$t\text{-}C_4H_9OH$	-14.67 ± 0.54 [b]

[a] In H_2O. Calculated from data in Table 1. [b] In H_2O+NaOH solution, from [2]. [c] In H_2O+LiOH solution. [d] In H_2O, from [2].

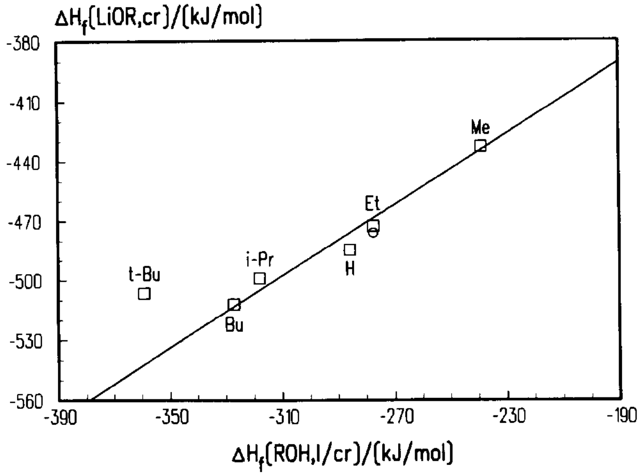


Fig. 1. Standard molar enthalpies of formation of lithium alkoxides versus the standard molar enthalpies of formation of the corresponding alcohols. Data from reaction (1) (squares) and from reaction (2) (circle).

apparently would affect all the enthalpy of formation data in Table 3. However, as is evident from eqn. 3, the enthalpies of formation of the lithium alkoxides depend also on the value of ΔH_{d2}, which was calculated as the difference $\Delta H_f^0(\mathrm{LiOH}:\infty\mathrm{H_2O}) - \Delta H_f^0(\mathrm{LiOH, cr}) = -23.55$ kJ/mol [4a], whereas the same difference in ref. 4b is calculated to be -21.41 kJ/mol. Therefore the discrepancy between the ΔH_{d2} values from the two sources is 2.14 kJ/mol, very close to the above difference in ΔH_f^0(LiOH, cr), so that the values of the enthalpy of formation in Table 3 are not significantly affected by the choice of either set of data.

A plot of the enthalpies of formation of the crystalline lithium alkoxides against the enthalpies of formation of the corresponding alcohols in their standard reference state (*i.e.* their stable physical state at 298 K and 1 bar) is shown in Fig. 1. This type of plot has been used before to assess the reliability of thermochemical data for many families of compounds [6], including the sodium alkoxides [2]. In the present case a good linear correlation for n-alkoxides ($r = 0.9968$; uncertainty intervals are standard deviations) (eqn. (5)) is obtained.

$$\Delta H_f^0(\mathrm{LiOR, cr}) = (0.894 \pm 0.071)\Delta H_f^0(\mathrm{ROH, l}) - (221 \pm 20) \qquad (5)$$

The general pattern of the plot in Fig. 1 is similar to the one observed for the analogous sodium alkoxides [2], namely the values for R = H and ^{i}Pr approximately fit the line and the enthalpy of formation of LiO^{t}Bu is considerably higher than predicted by eqn. 5. As pointed out before [2], this destabilization enthalpy of LiO^{t}Bu (*ca.* 36 kJ/mol) is relative to the correspond-

$$\begin{tikzcd}
\mathrm{LiOEt(cr)} + \arrow[d, "\Delta H_r"] & \mathrm{HCl \cdot 552H_2O} \arrow[r, "\Delta H_r^0"] \arrow[d, "\Delta H_{d4}=0"] & \mathrm{LiCl(cr)} + \arrow[d, "\Delta H_{d5}"] & \mathrm{EtOH(l)} + \arrow[d, "\Delta H_{d6}"] & \mathrm{552H_2O(l)} \arrow[d, "552\Delta H_{d7}"] \\
 & \text{Solution A} \arrow[rr, "\Delta H=0"] & & \text{Solution B} &
\end{tikzcd}$$

Solution A = Solution B = LiCl(sln) + EtOH(sln) + $n(\mathrm{HCl \cdot 552H_2O})$

Scheme 2.

TABLE 3. Reaction enthalpies and enthalpies of formation (in kJ/mol)

R	ΔH_r [a]	ΔH_f^0(LiOR, cr) [a]
CH_3	−36.0 ±2.3	−433.0 ±2.4
C_2H_5	−37.8 ±2.4	−473.0 ±2.5
	−87.8 ±3.8 [b]	−477.1 ±4.0 [b]
i-C_3H_7	−54.6 ±1.0	−499.3 ±1.4
C_4H_9	−45.34±0.69	−512.33±0.89
t-C_4H_9	−87.9 ±2.0	−508.6 ±2.2
2-C_5H_{11}		(−524.1 ±7.8) [c]
C_8H_{17}		(−537.1 ±7.8) [c]

[a] From data obtained for reaction (1), unless stated otherwise. [b] From data obtained for reaction (2). [c] Estimated according to eqn. (13).

$$\begin{tikzcd}
\mathrm{LiOR(cr)} + \mathrm{H_2O(l)} \arrow[r, "\Delta H_r^0"] \arrow[d, "\Delta H^0_{\mathrm{sub1}}"'] & \mathrm{ROH(l)} + \mathrm{LiOH(cr)} \arrow[d, "\Delta H^0_{\mathrm{sub2}}"] \\
\mathrm{LiOR(g)} + \mathrm{H_2O(g)} \arrow[r, "\Delta H_g^0"] & \mathrm{ROH(g)} + \mathrm{LiOH(g)}
\end{tikzcd}$$

$\Delta H^0_{\mathrm{vap1}}$ (H₂O(l) → H₂O(g)); $\Delta H^0_{\mathrm{vap2}}$ (ROH(l) → ROH(g))

Scheme 3.

ing ᵗBuOH, *i.e.* it reflects the effect of replacing a hydrogen atom by a lithium atom.

An interpretation of Fig. 1 can be seen in Scheme 3 or eqns. (6) and (7), where $\Delta H^0_{\mathrm{sub}}$ and $\Delta H^0_{\mathrm{vap}}$ are enthalpies of sublimation and vaporization, respectively, ΔH_g^0 is the enthalpy of reaction with all the reactants and products in the gas phase, and *D*(Li–OR), *D*(H–OH), *D*(RO–H), and *D*(Li–OH) are bond dissociation enthalpies.

$$\Delta H_f^0(\mathrm{LiOR, cr}) = \Delta H_f^0(\mathrm{ROH, l}) + \Delta H_f^0(\mathrm{LiOH, cr}) - \Delta H_f^0(\mathrm{H_2O, l}) - \Delta H_r^0 \qquad (6)$$

$$\begin{aligned}\Delta H_r^0 &= \Delta H_g^0 + \left(\Delta H^0_{\mathrm{sub1}} - \Delta H^0_{\mathrm{sub2}}\right) + \left(\Delta H^0_{\mathrm{vap1}} - \Delta H^0_{\mathrm{vap2}}\right)\\ &= D(\mathrm{Li{-}OR}) - D(\mathrm{RO{-}H}) + D(\mathrm{H{-}OH}) - D(\mathrm{Li{-}OH}) + \Delta\left(\Delta H^0_{\mathrm{sub}}\right) + \Delta\left(\Delta H^0_{\mathrm{vap}}\right) \qquad (7)\end{aligned}$$

A perfect unit-slope straight line in Fig. 1 would imply a constant value of ΔH_r^0 for the alkoxides that fit the linear correlation. This is approximately observed by eqn. (5) (the slope is slightly smaller than expected but this may result simply from the limited accuracy of our experimental values). If, on the other hand, one assumes that the differences between the sublimation, $\Delta(\Delta H^0_{\mathrm{sub}})$, and the vaporization enthalpies, $\Delta(\Delta H^0_{\mathrm{vap}})$, cancel each other [6], eqn. (7) leads to the conclusion that the difference *D*(Li–OR) − *D*(RO–H) is approximately constant for the lithium n-alkoxides. This conclusion can be used to estimate a rough value of *D*(Li–OR), since RO–H bond dissociation enthalpies fall in a narrow range [7]. A mean value, ⟨*D*(RO–H)⟩ = 435 ± 3 kJ/mol, together with *D*(HO–H) = 499 kJ/mol, *D*(Li–OH) = 436.42 kJ/mol [4a], and auxiliary data from Table 1, lead to ⟨*D*(Li–OR)⟩ ≅ 394 kJ/mol. Recall that this value is applicable to the alkoxides that fit the correlation in Fig. 1.

An explanation for the "high" value of ΔH_f^0(LiOᵗBu, cr) relative to the n-alkoxide trend may be tied to differences in the solid state structures of the lithium alkoxides, which unfortunately are not available [8]. These could possibly also explain the deviation of the slope from the predicted value (unity). As remarked before [2], ionic-type structures may be favoured for smaller alkyl groups, relative to longer or bulky alkyl chains. Steric effects were considered a less likely explanation for the destabilization of NaOᵗBu in our studies involving the sodium alkoxides [2]. Interestingly, the destabilization observed for NaOᵗBu (19 kJ/mol) is smaller than that derived for LiOᵗBu (36 kJ/mol).

While crystal packing effects may be responsible for the high enthalpies of formation of NaOᵗBu and LiOᵗBu, we have decided to use a simple electronegativity model to investigate if the change in the ionic character of M–OR bond (M = Li or Na) with different R groups would account, at least qualitatively, for those deviations. That model relies on two assumptions: (1) M–OR and RO–H bond dissociation enthalpies can be regarded as the sum of two contributions, covalent and ionic; (2) the ionic term is proportional to the electronegativity (χ) of the alkoxy group, which has different values in MOR and ROH. On these bases, eqns. (8a) and (8b) can be written.

$$D(\mathrm{M{-}OR}) = D_{\mathrm{cov}} + D_{\mathrm{ion}} = D_{\mathrm{cov}} + \alpha\chi_{\mathrm{RO(M)}} \qquad (8a)$$

$$D(\mathrm{RO{-}H}) = D'_{\mathrm{cov}} + D'_{\mathrm{ion}} = D'_{\mathrm{cov}} + \alpha\chi_{\mathrm{RO(H)}} \qquad (8b)$$

A constant value of α for the alkoxy family is also assumed in our model, implying that the change in the ionic contribution is totally reflected by the electronegativity value. As bond dissociation enthalpies can also be expressed in terms of the enthalpies of formation of the species involved (eqns. (9a) and (9b)), it is possible to derive eqn. (10), which gives ΔH_f^0(MOR) as a function of ΔH_f^0(ROH) and the difference between the electronegativities of RO in the alcohol and the metal alkoxide, $[\chi_{\mathrm{RO(H)}} - \chi_{\mathrm{RO(M)}}]$. The remaining terms in this equation are either constant [ΔH_f^0(M) and ΔH_f^0(H)] or assumed to be constant $(-D_{\mathrm{cov}} + D'_{\mathrm{cov}})$.

$$D(\mathrm{M{-}OR}) = \Delta H_f^0(\mathrm{M}) + \Delta H_f^0(\mathrm{RO}) - \Delta H_f^0(\mathrm{MOR}) \qquad (9a)$$

$$D(\mathrm{RO{-}H}) = \Delta H_f^0(\mathrm{H}) + \Delta H_f^0(\mathrm{RO}) - \Delta H_f^0(\mathrm{ROH}) \qquad (9b)$$

TABLE 4. Group electronegativities of several alkoxide groups in LiOR, NaOR and ROH

R	$\chi_{RO(H)}$	$\chi_{RO(Li)}$	$\chi_{RO(H)}-\chi_{RO(Li)}$	$\chi_{RO(Na)}$	$\chi_{RO(H)}-\chi_{RO(Na)}$
Me	7.69	5.41	2.28	5.39	2.30
Et	7.69	6.06	1.63	6.03	1.66
^{i}Pr	7.67	6.40	1.27	6.38	1.29
Bu	7.65	6.57	1.08	6.55	1.10
^{t}Bu	7.65	6.61	1.04	6.59	1.06
2-C_5H_{11}	7.65	6.76	0.89	6.74	0.91
C_8H_{17}	7.62	7.01	0.61	7.00	0.62

$$\Delta H_f^0(\text{MOR}) = \Delta H_f^0(\text{ROH}) - \Delta H_f^0(\text{M}) - \Delta H_f^0(\text{H}) - D_{\text{cov}} + D'_{\text{cov}} + \alpha[\chi_{\text{RO(H)}} - \chi_{\text{RO(M)}}] \quad (10)$$

In order to verify if the experimental data are fit by the above model, the electronegativities of the various alkoxide groups were calculated by the method described in the Appendix. These electronegativity data were collected in Table 4 and used to make a multiple linear regression of ΔH_f^0(MOR, cr) as a function of ΔH_f^0(ROH, l) and $(\chi_{\text{RO(H)}} - \chi_{\text{RO(M)}})$. In the case of the lithium alkoxides, the empirical correlation obtained for R = Me, Et, ^{i}Pr, Bu and ^{t}Bu (eqn. 11, $r = 0.9982$, standard error of estimate = 3.9 kJ/mol) can be compared, not with eqn. (5) (that only considers R = Me, Et, and Bu) but with eqn. (12) ($r = 0.9475$), which was derived by using the data for the five alkoxides, without the electronegativity term.

$$\Delta H_f^0(\text{LiOR, cr}) = -(0.12 \pm 0.16)\Delta H_f^0(\text{ROH, l}) + (75 \pm 14)(\chi_{\text{RO(H)}} - \chi_{\text{RO(Li)}}) - (634 \pm 68) \quad (11)$$

$$\Delta H_f^0(\text{LiOR, cr}) = (0.67 \pm 0.13)\Delta H_f^0(\text{ROH, l}) - (281 \pm 40) \quad (12)$$

TABLE 5. Lattice energies of lithium alkoxides. Estimates of enthalpies of sublimation and heterolytic Li^+–OR^- bond dissociation enthalpies (in kJ/mol)

R	ΔH_f^0(RO, g) [a]	*EA*(RO) [b]	U_0 [c]	D_{het}	ΔH_{sub}^0
H	39 ± 4	176.4 ± 1.0	1028.4 ± 4.1	786.4	247.0
Me	18 ± 4	151.4 ± 2.1	980.4 ± 5.1	769	216
Et	−17 ± 4	166.5 ± 3.2	970.3 ± 5.7	753	222
^{i}Pr	−52 ± 4	177.4 ± 2.8	950.6 ± 5.1	743	213
Bu	−63 ± 4	171 ± 14	959 ± 15	749	215
^{t}Bu	−91 ± 5	184.4 ± 5.2	914.0 ± 7.5	736	183

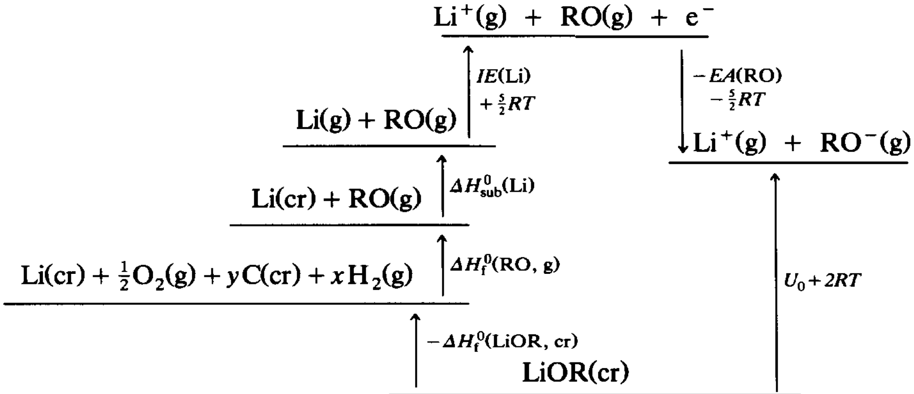
[a] Data from [7]. [b] Data from [13]. [c] *IE*(Li) = 526.41 kJ/mol and ΔH_{sub}^0(Li) = 159.37 kJ/mol [4(a)].

The correlation coefficient of eqn. (11) is greatly improved relative to eqn. (12), suggesting that an electronic effect can be responsible, at least, in part, for the deviation of LiO^{t}Bu and LiO^{i}Pr enthalpies of formation from the line in Fig. 1. It is stressed that there is an increase of degrees of freedom from eqn. (5) to eqn. (11). It is also noted that although the error bars in eqn. (11) are quite high, specially in the third term, this is due in part to the rather negative enthalpies of formation of the alcohols, implying a long extrapolation to obtain the intercept. As indicated above, the standard error of the estimate is only 3.9 kJ/mol, allowing the prediction of accurate values.

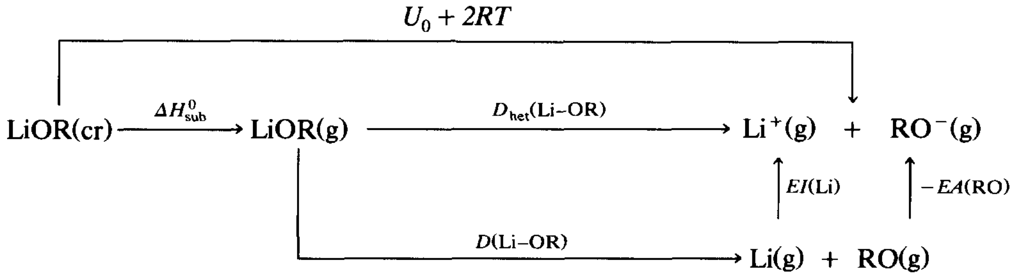
Similar calculations were performed with the enthalpies of formation of sodium alkoxides [2], and an improvement was also observed when the electronegativity term was included, eqns. (13) and (14) (R = Me, Et, ^{i}Pr, Bu and ^{t}Bu; $r = 0.9904$, standard error of estimation 12.1 kJ/mol, for eqn. (13); $r = 0.9781$ for eqn. (14)).

$$\Delta H_f^0(\text{NaOR, cr}) = (0.39 \pm 0.49)\Delta H_f^0(\text{ROH, cr/l}) + (50 \pm 44)(\chi_{\text{RO(H)}} - \chi_{\text{RO(Na)}}) - (393 \pm 213) \quad (13)$$

$$\Delta H_f^0(\text{NaOR, cr}) = (0.92 \pm 0.14)\Delta H_f^0(\text{ROH, cr/l}) - (158 \pm 42) \quad (14)$$



Scheme 4.



Scheme 5.

A good example of the use of eqn. (13) to predict data is provided by the enthalpies of formation of $NaOC_8H_{17}$ and $NaO\text{-}2\text{-}C_5H_{11}$. The estimated values, $\Delta H_f^0(NaOC_8H_{17}, cr) = -528.3$ kJ/mol and $\Delta H_f^0(NaO\text{-}2\text{-}C_5H_{11}, cr) = -490.0$ kJ/mol are in good agreement with the experimental data, -526.3 ± 4.8 and -485.9 ± 2.2 kJ/mol, respectively [2]. Equation (14) leads to a poorer agreement, $\Delta H_f^0(NaOC_8H_{17}, cr) = -550.4$ kJ/mol and $\Delta H_f^0(NaO\text{-}2\text{-}C_5H_{11}, cr) = -494.0$ kJ/mol. In conclusion, our simple empirical model, relying on straightforward calculations of group electronegativities, affords fairly accurate predictions of new data, and, as indicated above, it seems to indicate that electronic, rather than steric effects, are responsible for the "high" values of the enthalpies of formation of non-linear alkoxides.

The lattice energy, U_0, of the lithium alkoxides can be calculated from Scheme 4 by using the enthalpies of formation in Table 3. The values (Table 5) are rather high, only 50–100 kJ/mol lower than the lattice energy of lithium hydroxide, indicating a strong ionic nature of Li–OR bonds. This can perhaps be better appreciated when the lattice energy is decomposed in two terms, the enthalpy of sublimation of the lithium alkoxide, ΔH^0_{sub}(LiOR), and the Li–OR heterolytic bond dissociation enthalpy, D_{het}(Li–OR) (Scheme 5).

Estimates of D_{het}(Li–OR) for R = n-alkyl can be made by using the above value for ⟨D(Li–OR)⟩, 394 kJ/mol, together with the ionization energy of Li and the electron affinity of RO. The results (Table 5) were then used to derive the sublimation enthalpies of the alkoxides, also collected in Table 5. Although there are no experimental data for these quantities in the literature, a theoretical calculation by Sana *et al.* [9] of the enthalpy of formation of lithium methoxide, -213.8 ± 4.2 kJ/mol, agrees quite well with the one obtained by using the enthalpy of formation of crystalline lithium methoxide (Table 3) and its enthalpy of sublimation (Table 5), $\Delta H_f^0(\text{LiOMe}, g) = -217$ kJ/mol.

Assuming the ionic nature of lithium alkoxides, the thermochemical radii of the anions RO^- were calculated using the Kapustinskii approximation (eqn. (15)) [10,11]. Here, ν is the number of ions in one molecule, z_+ and z_- are the charges of Li^+ and RO^-, and r_+ and r_- are the respective thermochemical radii in pm. The results for r_- are presented in Table 6 and compared with the values derived earlier for the sodium alkoxides [2]. The good agreement between the two independent sets of data supports the reliability of the enthalpies of formation of sodium and lithium alkoxides determined here and in our earlier paper. Moreover, it also indicates that the Kapustinskii equation and the thermochemical radii in Table 6 can be used to calculate the lattice energies of other alkaline metal alkoxides and thus to estimate (Scheme 4) their standard enthalpies of formation.

$$U_0 = \frac{1.079 \times 10^5 \nu z_+ z_-}{r_+ + r_-} \qquad (15)$$

TABLE 6. Thermochemical radii of RO^- (pm) [a]

R	r_{therm} [b]	r_{therm} [c]
H	142	140
Me	152	154
Et	154	157
${}^iPr$	159	156
Bu	157	157
${}^tBu$	169	168

[a] $r_+(Li^+) = 68$ and $r_+(Na^+) = 102$ pm. [b] Data from lithium alkoxides. [c] Data from sodium alkoxides [2].

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Appendix

A considerable amount of work on electronegativity scales has been reported since 1932, when Pauling defined electronegativity as "the power of an atom in a molecule to attract electrons to itself" [14–26]. Nevertheless, most of the available scales refer only to bare atoms and those which deal with group electronegativity do not allow isomers to be distinguished [27].

The method proposed in the present paper is straightforward (calculations are made with a personal computer or a programmable calculator), allows differentiation between isomers and leads to different electronegativities for the same group in different environments [28].

The basis of the method is the equation proposed by Iczkowski and Margrave [18] (eqn. (16)), where E represents the electronic energy, χ the electronegativity, and δ the partial charge in an atom.

$$\chi = -(\partial E/\partial \delta)_{\delta=0} \tag{16}$$

The electronic energy of an atom can be expressed as a function of the charge (δ) of the atom (eqn. (17)), where α, β, γ, and ϵ are constants that depend on the atom and its valence state.

$$E(\delta) = \alpha\delta + \beta\delta^2 + \gamma\delta^3 + \epsilon\delta^4 \tag{17}$$

If only the first two terms are considered (eqn. (18)), the electronegativity reduces to the Mulliken definition (eqn. (19)).

$$E(\delta) = \alpha\delta + \beta\delta^2 \tag{18}$$

$$\chi = \alpha + 2\beta\delta \tag{19}$$

As eqn. (18) represents the energy of one atom with a partial charge δ, the electronic energy of a polyatomic molecule will be, to a first approximation, the sum of several $E(\delta)$. However, the different atomic charges will create dipoles, so that an electrostatic term should be added for each bond in the molecule. This electrostatic term is given by eqn. (20), where k is $1/4\pi\epsilon_0$, δ_i is the charge of each atom, d the distance between each two bonded atoms and N the number of atoms in the molecule.

$$E_e = \frac{k}{N}\cdot\frac{\delta_1\delta_2}{d} \qquad (20)$$

The "total" electronic energy of a polyatomic molecule is, therefore,

$$E=\sum_{i=1}^{N}\left(a_i\delta_i+\frac{b_i}{2}\delta_i^2\right)+\sum_{\substack{i,j\\ \text{bonded}}}\frac{k}{N}\frac{\delta_i\delta_j}{d_{ij}} \qquad (21)$$

where $a_i \equiv \alpha_i$ and $b_i = 2\beta_i$ for each atom. The minimization of the total electronic energy given by eqn. (21) leads to the values of charges in all atoms of the molecule. This minimization procedure is iterative: initial values of δ_i are assumed for all the atoms (bearing in mind that their sum must be zero), and then the effect of changing δ_i on the total energy is analysed.

Once the set of δ_i that minimizes E is obtained, the electronegativity of a given group (*e.g.* RO) is identified with the electronegativity of the atom that is bonded to the other part of the molecule (*e.g.* H, Na, or Li). The electronegativity of that atom (oxygen) can be calculated using eqn. (22).

$$\chi = a_i + b_i\delta_i \qquad (22)$$

For the calculations presented in this paper, values of a_i and b_i derived by Bratsch [29] were used (Table 7). The distances and angles needed were taken from ref. 30 or estimated.

As the previous method affords the charge distribution in a molecule, it enables one to calculate dipole moments. This has been done for a few molecules and the results compared with experimental data and with SCF-MNDO results (Table 8). Despite the extreme simplicity of the method, the agreement is generally satisfactory.

A number of electronegativity values calculated by our method were compared (Fig. 2) to those reported in a recent paper by Allen and Reed [24b]. These authors have derived the so-called bond polarity index, BPI, for a series of groups attached to methyl, and found that this parameter correlates well with several experimental quantities. Although some dispersion can be observed in Fig. 2, the correlation ($r = 0.938$) is satisfactory.

TABLE 8. Calculated and experimental dipole moments for simple molecules (Debye)

Molecule	μ(exp)	μ(calc) [a]	μ(MNDO) [b]
HF	1.91	1.50	1.95
HCl	1.04	1.03	1.32
HBr	0.79	0.77	1.01
HI	0.42	0.48	1.04
H_2O	1.85	1.61	1.79
H_2S	0.94	0.86	1.58
MeOH	1.71	1.57	1.65

[a] Calculated by the method described in the Appendix. [b] Calculated for the experimental geometry.

TABLE 7. Values of a_i and b_i considered in the calculations

	V [a]	VS [b]	a_i [c]	b_i [c]
H	1	s	7.176	12.844
Li	1	s	3.005	4.774
B	3	33.3%s	6.37	8.74
C	4	50%s	10.42	11.70
		33.3%s	8.91	11.50
		25%s	8.15	11.39
N	3	50%s	14.00	13.32
		33.3%s	11.78	13.22
		25%s	10.66	13.16
O	2	25%s	14.02	15.55
		16.7%s	12.55	15.47
F	1	14.3%s	15.30	17.81
		p	12.202	17.572
Na	1	s	2.844	4.591
Si	4	25%s	7.30	7.13
S	2	16.7%s	9.04	10.28
Cl	1	14.3%s	10.95	11.55
		p	9.350	11.395

[a] V = valence. [b] VS = valence state. [c] Data from [29].

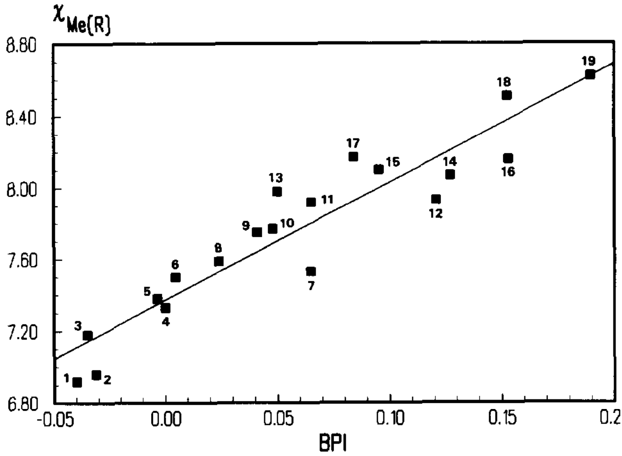

Fig. 2. Correlation between group electronegativities calculated by the method described in this paper and bond polarity indexes [24(b)]. 1-BH_2, 2-H, 3-SiH_3, 4-Me, 5-Et, 6-CH_2NH_2, 7-SH, 8-CH_2OH, 9-CH_2F, 10-NH_2, 11-CHO, 12-Cl, 13-CCH, 14-CF_3, 15-OH, 16-CN, 17-COOH, 18-NO_2, 19-F.