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Thermochemistry of Li, Na, K, Rb and Cs alkylated phenoxides

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Abstract

Lattice energies and thermochemical radii of the anions OR^- (R = 2-Me; 2,6-Me$_2$; 2,4,6-Me$_3$; 2,6-t-Bu$_2$) in alkali metal phenoxides, MOR (M = Li, Na, K, Rb and Cs) were investigated based on the corresponding standard molar enthalpies of formation determined by reaction–solution calorimetry. The results obtained at 298.15 K were as follows: $\Delta_f H_m^\circ$ (MOR, cr)/kJ mol^{-1} = −398.4 ± 1.1 (LiO-2-MePh), −423.4 ± 1.6 (LiO-2,6-Me$_2$Ph), −457.3 ± 7.1 (LiO-2,4,6-Me$_3$Ph), −346.6 ± 1.4 (NaO-2-MePh), −399.1 ± 1.5 (NaO-2,6-Me$_2$Ph), −422.4 ± 7.1 (NaO-2,4,6-Me$_3$Ph), −496.6 ± 7.1(NaO-2,6-t-Bu$_2$Ph), −367.8 ± 1.2 (KO-2-MePh), −399.1 ± 1.4 (KO-2,6-Me$_2$Ph), −368.8 ± 1.2 (RbO-2-MePh), −403.6 ± 1.3 (RbO-2,6-Me$_2$Ph), −387.0 ± 1.6 (CsO-2-MePh) and −413.6 ± 1.3 (CsO-2,6-Me$_2$Ph). Estimates of thermochemical raddi, lattice energies and standard enthalpies of formation of not experimentally measured alkali metal phenoxides was successfully done with a model based on the Kapustinskii equation and the set of values experimentally determined.
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1. Introduction

Although important in synthetic chemistry, there is little knowledge of alkali metal phenoxide thermochemical data [1]. Phenoxides commonly act as strong bases or nucleophilic agents [2]. The most important one at an industrial scale is sodium phenoxide. It is the starting material for the Kolbe–Schmitt process (carboxylation of NaOPh by a stream of CO$_2$) and has been used to produce salicylic acid since 1874 [3,4]. They are also industrially relevant, for example, as additives to improve the temperature and pressure resistance of mineral lubricating oils and to minimise the corrosive properties of detergents [4].

Thermochemical data previously reported on [5] consider only the phenol group without substituents. The substituent effect of methyl and terbutyl groups is the main objective of this paper.

2. Experimental

2.1. Materials

2-Methylphenol (Aldrich, 99%) was dried over calcium hydride and distilled. 2,6-Dimethylphenol, 2,4,6-trimethylphenol and 2,6-diterbutylphenol all from Aldrich with 99% purity were sublimed twice. Lithium (Merck, >99%), sodium (Riedel–deHaën) and potassium (Merck, >99%) were used as small pieces. The oxidized surface was removed inside a glove box. Rubidium and cesium (Aldrich, +99.95%) were used as supplied and stored in an oxygen and water free glove box. Sodium hydroxide (Riedel–deHaën, minimun 99%) and potassium hydroxide (Pronalab) were used as supplied. THF was pre-dried over 4 Å molecular sieves and distilled under sodium. Pentane was pre-dried under calcium sulphate and distilled over P$_2$O$_5$.

2.2. Physical measurements

Infrared spectra were determined with a Bruker Tensor 27 spectrophotometer with samples mounted as Nujol mulls

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between CsI plates. Elemental analyses were performed on a CE Instruments EA1110 CHNS-O automatic analyzer (C and H) or by titration (M).

2.3. Phenoxides synthesis

All synthesis were carried out inside an oxygen and water free (<5 ppm) glove-box. THF and pentane were degassed before use. 2-Methylphenol, 2,6-dimethylphenol, 2,4,6-trimethylphenol or 2,6-terbutylphenol, was added to a stirred suspension of small pieces of the appropriate metal in THF. For lithium, sodium and potassium derivatives an excess of metal was used. The mixture was stirred for about 5 h until hydrogen evolution stopped. The reaction solution was filtered to ensure that unreacted chunks were removed. The remaining suspension was taken to dryness. The white solid was ground and washed with aliquots of pentane. The pentane suspension was centrifuged and the liquid removed. The washed solid compound was transferred to a schlenk tube and dried in vacuum at room temperature. The compound was further dried in high vacuum during eight hours. A similar method was followed in the preparation of the rubidium and cesium methylphenoxides although instead of an excess of metal, an excess of 2-methylphenol or 2,6-dimethylphenol was used.

2.4. Reaction–solution calorimetry

The enthalpies of formation of the phenoxides were determined by measuring the enthalpies of reaction and solution in water, except for sodium 2,6-diterbutyl phenoxide. For this compound the reaction in a mixture of ethanol and water (168 ml of ethanol and 2 ml of distilled and deionised water) was preferred due to the low solubility of 2,6-diterbutylphenol in water. The calorimeter was specially built for the study of oxygen and water sensitive compounds, and the experimental procedure was described in a previous paper [6]. In the present work the reaction vessel is a 220 ml Dewar flask filled with 170 ml of the appropriate reaction media. All measurements were made near 298.15 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

3.1. Elemental analysis (%) and infrared spectra (Nujol, $\nu\,cm^{-1}$)

Li(O-2-MePh) (114.072): C 73.70, H 6.19, Li 6.08; found: C 73.22, H 7.59, Li 6.51; IR (Nujol, $\nu\,cm^{-1}$): 1591 (vs), 1559 (w), 1482 (vs), 1458(vs), 1377 (s), 1289 (vs), 1045 (s), 862 (w), 756 (s), 720 (s), 669 (w), 598 (w), 558 (w), 483 (w), 399 (s), 280 (w), 247 (vw).

Na(O-2-MePh) (130.120): C 64.61, H 5.42, Na 17.67; found: C 64.47, H 5.35, Na 16.81; IR (Nujol, $\nu\,cm^{-1}$): 1591 (s), 1559 (w), 1480 (vs), 1458 (vs), 1440 (vs), 1377 (s), 1276 (vs), 1109 (w), 1047 (w), 852 (w), 800 (w), 759 (s), 729(w), 546 (vw), 464 (vw), 335 (vw), 279 (w), 247 (w).

K(O-2-MePh) (146.229): C 57.50, H 4.83, K 26.74 found: C 57.85, H 4.42, K 27.75; IR (Nujol, $\nu\,cm^{-1}$): 1584 (s), 1463 (vs), 1376 (s), 1306 (s), 1043 (w), 858 (w), 766 (w), 541 (vw), 458 (w), 325 (w), 279 (vw), 247 (w).

Rb(O-2-MePh) (192.598): C 43.65, H 3.66, Rb 44.38; found: C 43.97, H 4.01, Rb 45.62; IR (Nujol, $\nu\,cm^{-1}$): 1585 (s), 1544 (w), 1465 (vs), 1377 (s), 1312 (s), 1261 (w), 1171 (w), 1103 (w), 1042 (w), 855 (w), 800 (w), 764 (s), 732(w), 539 (vw), 459 (vw), 324 (vw), 279 (vw).

Cs(O-2-MePh) (240.036): C 35.03, H 2.94, Cs 55.37; found: C 37.94, H 3.65, Cs 55.09; IR (Nujol, $\nu\,cm^{-1}$): 1583 (w), 1458 (vs), 1376 (s), 1260 (s), 1118 (w), 1047 (vw), 800 (w), 759 (w), 729(w), 539 (vw), 457 (vw), 326 (vw), 303 (vw), 279 (vw), 247 (vw).

Li(O-2,6-Me$_2$Ph) (128,098): C 75.01, H 7.08, Li 5.42; found: C 75.01, H 7.47, Li 5.33; IR (Nujol, $\nu\,cm^{-1}$): 1589 (s), 1464 (vs), 1430 (vs), 1376 (vs), 1279 (vs), 1237 (s), 1194 (w), 1093 (vs), 1041 (vs), 979 (w), 915 (w); 890 (w), 849 (s), 800 (w), 766 (s), 751 (s), 689 (w), 577 (vw), 526 (w), 502 (w),418 (w), 327 (vw), 303 (vw), 247 (vw).

Na(O-2,6-Me$_2$Ph) (144.147): C 66.66, H 6.29, Na 15.95; found: C 66.42, H 7.49, Na 15.89 IR (Nujol, $\nu\,cm^{-1}$): 1590 (s), 1465 (vs), 1430 (vs), 1376 (vs), 1326(w), 1290 (vs), 1237 (s), 1092 (vs), 1045 (vs), 974 (w), 911 (w), 845 (s), 801 (w), 767 (s), 748 (s), 684 (w), 504 (w), 354 (vw), 247 (vw).

K(O-2,6-Me$_2$Ph) (160.256): C 59.96, H 5.66, K 24.40; found: C 59.07, H 5.94, K 24.62 IR (Nujol, $\nu\,cm^{-1}$): 1584 (s), 1459 (vs), 1376 (vs), 1307 (s), 1261 (s), 1087 (s), 1019 (s), 845 (s), 800 (w), 757 (s), 722 (s), 668 (w), 500 (vw), 352 (vw) 326 (vw), 302 (vw), 247 (vw).

Rb(O-2,6-Me$_2$Ph) (206.625): C 46.50, H 4.39, Rb 41.36; found: C 46.46, H 4.36, Rb 41.49 IR (Nujol, $\nu\,cm^{-1}$): 1584 (s), 1464 (vs), 1427 (vs), 1376 (vs), 1312 (s), 1261 (s), 1087 (s), 1019 (s), 844 (s), 800 (w), 752 (s), 669 (vw), 496 (vw), 328 (vw), 302 (vw), 247 (vw).

Cs(O-2,6-Me$_2$Ph) (254.063): C 37.82, H 3.57, Cs 52.31; found: C 39.19, H 4.26, Cs 51.67 IR (Nujol, $\nu\,cm^{-1}$):): 1584 (s), 1463 (vs), 1376 (vs), 1337 (s), 1316 (s), 1261 (s), 1085 (s), 1018 (s), 843 (s), 800 (w), 752 (s), 669 (vw), 494 (vw), 325 (vw), 302 (vw), 247 (vw).

Li(O-2,4,6-Me$_3$Ph) (142.125): C 76.06, H 7.80, Li 4.88; found: C 76.46, H 7.90, Li 4.20 IR (Nujol, $\nu\,cm^{-1}$): 1479 (vs), 1377 (s), 1310 (vs), 1262 (vs), 1155 (w), 1093 (w), 1017 (s), 957 (w), 868 (w), 801 (s), 602 (w), 514 (w), 425 (w), 351 (vw), 293 (vw), 280 (vw).

Na(O-2,4,6-Me$_3$Ph) (158.174): C 68.34, H 7.01, Na 15.31; found: C 68.54, H 7.23, Na 15.98 IR (Nujol, $\nu\,cm^{-1}$): 1465 (vs), 1377 (vs), 1309 (vs), 1258 (vs), 1154 (s), 1093 (s), 1018 (s), 955 (w), 860 (s), 798 (vs), 600 (w), 577 (w), 477 (s), 376 (w), 352 (w), 302 (vw), 280 (vw).

Na(O-2,6-t-BuPh) (228.307): C 73.65, H 9.27, Na 10.07; found: C 73.56, H 11.48, Na 10.87 IR (Nujol, $\nu\,cm^{-1}$): 1574 (s), 1543 (w), 1459 (vs), 1411 (vs), 1375 (vs), 1356 (vs), 1291
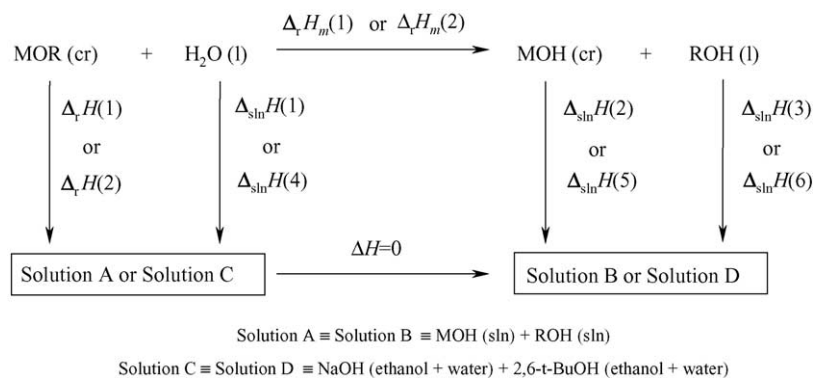
Scheme 1. $\Delta_r H_m^\circ(1)$ represents the enthalpy change for the reaction of MOR with distilled and deionised water, and $\Delta_r H_m^\circ(2)$ the reaction enthalpy of sodium 2,6-terbutyl phenoxide in the ethanol/water mixture, with all the compounds in its standard state. $\Delta_r H(1)$ and $\Delta_r H(2)$ stand for the measured reaction enthalpies under the experimental conditions; $\Delta_{s1n}(2)$ the enthalpy change due to the dissolution of stoichiometric amounts of MOH in H_2O, $\Delta_{s1n}(3)$ the enthalpy change due to the dissolution of 2-methyl-phenol, 2,6-dimethyl-phenol or 2,4,6-trimethyl-phenol in H_2O + MOH, $\Delta_{s1n}(5)$ dissolution enthalpy of NaOH in ethanol/water mixture, $\Delta_{s1n}(6)$ the enthalpy change due to the dissolution of 2,6-terbuthyl-phenol in ethanol/water/NaOH mixture. $\Delta_{s1n}(1)$ is the term referring the dissolution of water in water that is obviously zero. $\Delta_{s1n}(4)$ is the dissolution of water in the ethanol/water mixture that after evaluation is not significant and assumed equal to zero [11].

(vs), 1258 (vs), 1230 (s), 1198 (s), 1144 (s), 1095 (vs), 1019 (s), 946 (w), 923 (w), 879 (w), 855 (w), 807 (w), 764 (s), 746 (w), 630 (w), 530 (w), 466 (w), 434 (w), 378 (w), 335 (w), 295 (w).

3.2. Calorimetric measurements

The enthalpies of formation of lithium, sodium, potassium, rubidium and cesium 2-methyl and 2,6-dimethyl phenoxides, as well as lithium and sodium 2,4,6-trimethyl and

Table 1
Auxiliary data ($T = 298.15$ K)

Compound	$\Delta_f H_m^\circ$ (kJ mol^{-1})	Reference
H_2O, l	-285.830 ± 0.04	[7]
2-MeOPh, l	-204 ± 1	[8]
2,6-Me$_2$OPh, l	-237 ± 1	[8]
2,4,6-Me$_3$OPh, l	-270 ± 7	[9]
2,6-t-Bu$_2$OPh, l	-370 ± 7	[9]
LiOH, cr	-483.93 ± 0.08	[7]
LiOH, ai	-508.48	[7]
LiOH·1000000H$_2$0	-508.444 ± 0.08	[7]
Li, g	159.37 ± 0.08	[7]
NaOH, cr	-425.609 ± 0.008	[7]
NaOH, ai	-470.114	[7]
NaOH·∞H$_2$O	-470.11 ± 0.08	[7]
Na, g	107.32 ± 0.08	[7]
KOH, cr	-424.764 ± 0.008	[7]
KOH, ai	-482.37 ± 0.08	[7]
KOH·∞H$_2$O	-482.37 ± 0.08	[7]
K, g	89.24 ± 0.08	[7]
RbOH, cr	-418.1 ± 0.08	[7]
RbOH, ai	-481.16 ± 0.08	[7]
RbOH·200H$_2$O	-480.32 ± 0.08	[7]
Rb, g	80.88 ± 0.08	[7]
CsOH, cr	-417.23 ± 0.08	[7]
CsOH·50000 H$_2$O	-488.1 ± 0.08	[7]
Cs, g	76.065 ± 0.008	[7]

sodium 2,6-diterbutyl phenoxides were calculated according to Scheme 1. Table 1 [7,8,9] presents the auxiliary enthalpy of formation data used in calculations. The molar quantities are based on the 2001 standard atomic masses [10].

As the concentration of MOH in solution is always very small (1 mol of LiOH in 10^6 mol of water or 1 mol of CsOH in 10^7 mol of water) infinite dissolution conditions can be assumed. From this it follows that $\Delta_{s1n}H(2)$ can be calculated as: 24.51 ± 0.08 kJ mol^{-1} (LiOH), -44.50 ± 0.08 kJ mol^{-1} (NaOH), -57.61 ± 0.08 kJ mol^{-1} (KOH), -62.13 ± 0.11 kJ mol^{-1} (RbOH) and -70.96 ± 0.11 kJ mol^{-1} (CsOH), based on $\Delta_f H_m^\circ$ (MOH, cr) and $\Delta_f H_m^\circ$ (MOH·∞H$_2$O), data reported in literature [7]. $\Delta_{s1n}H(5)$ was experimentally measured in this work.

$\Delta_{s1n}H(3)$ Values for 2-methyl-phenol, 2,6-dimethyl-phenol and 2,4,6-terbutyl-phenol were experimentally obtained in this work. Dissolutions in water and MOH with M = Li, Na, K for 2-methyl-phenol and 2,6-dimethyl-phenol were made. For rubidium and cesium compounds the $\Delta_{s1n}H(3)$ value of potassium was used. $\Delta_{s1n}H(6)$ was also determined, in this case the dissolution of 2,4,6-terbuthyl-phenol was made in ethanol/water/NaOH solution. It should be noted that the amount of MOH in solution was always kept in the order of the concentration needed to simulate the solution B or D (Scheme 1, Table 2.).

From Scheme 1 it was possible to calculate the enthalpies of formation of the phenoxides using Eq. (1), or Eq. (2) in the case of 2,6-terbutyl sodium phenoxide. The obtained values are presented in Table 3.

$$\Delta_f H_m^\circ(\text{MOR}) = \Delta_f H_m^\circ(\text{MOH, cr}) + \Delta_f H_m^\circ(\text{ROH, l})$$
$$- \Delta_f H_m^\circ(H_2O, l) - \Delta_r H(1)$$
$$+ \Delta_{s1n}H(2) + \Delta_{s1n}H(3) \qquad (1)$$

Table 2
Dissolution enthalpies ($T = 298.15$ K)

Compound	$\Delta_{sln}H_{(3)}$ (kJ mol^{-1})				$\Delta_{sln}H_{(5)}$ or $\Delta_{sln}H_{(6)}$ (kJ mol^{-1})
2-MeOPh	13.7 ± 0.6[a]	14.9 ± 0.4[b]	12.1 ± 0.7[c]	9.3 ± 0.4[d]	
2,6-Me$_2$OPh	13.8 ± 0.3[a]	15.3 ± 1.2[b]	1.0 ± 0.7[c]	4.6 ± 0.5[d]	
2,4,6-Me$_3$OPh				3.1 ± 0.5[d]	
2,6-t-Bu$_2$OPh					11.5 ± 0.2[e]
NaOH					-55.2 ± 0.9[f]

[a] Dissolution in water.
[b] Dissolution in water and LiOH.
[c] Dissolution in water and NaOH.
[d] Dissolution in water and KOH.
[e] Dissolution in ethanol + water + NaOH.
[f] Dissolution in ethanol + water.

$$\Delta_f H_m^\circ[\text{Na(O-2, 6-}t\text{-Bu), cr}]$$
$$= \Delta_f H_m^\circ[\text{NaOH, cr}] + \Delta_f H_m^\circ(2, 6\text{-}t\text{-BuOH, l})$$
$$- \Delta_f H_m^\circ(\text{H}_2\text{O, l}) - \Delta_r H(2) + \Delta_{sln}H(5) + \Delta_{sln}H(6)$$
$$(2)$$

The calculation of lattice energies ($\Delta_{lat}U^\circ$) of lithium, sodium, potassium, rubidium and cesium phenoxides can be done if an ionic nature for MOPh in the solid state is assumed. In this case ($\Delta_{lat}U^\circ$) (MOR) should be defined as the internal energy change associated with the following process [12].

$$\text{MOR(cr)} \rightarrow \text{M}^+(\text{g}) + \text{RO}^-(\text{g}) \qquad (3)$$
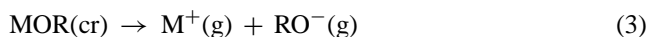
where M is alkali metal; R is phenyl group.

To evaluate this quantity Scheme 2 can be used. Eq. (4), obtained directly from Scheme 2, allows computation of $\Delta_{lat}U_{298}^\circ$ (MOR), the internal energy change associated with Eq. (3) at 298.15 K, where R is the gas constant, T the absolute temperature, $\Delta_{sub}H_m^\circ$ (M) and $\Delta_i H_m^\circ$ (M) the enthalpy of sublimation and the enthalpy of ionisation of the metal, respectively, and $\Delta_{ea}H_m^\circ$ (OR) the enthalpic electron affinity
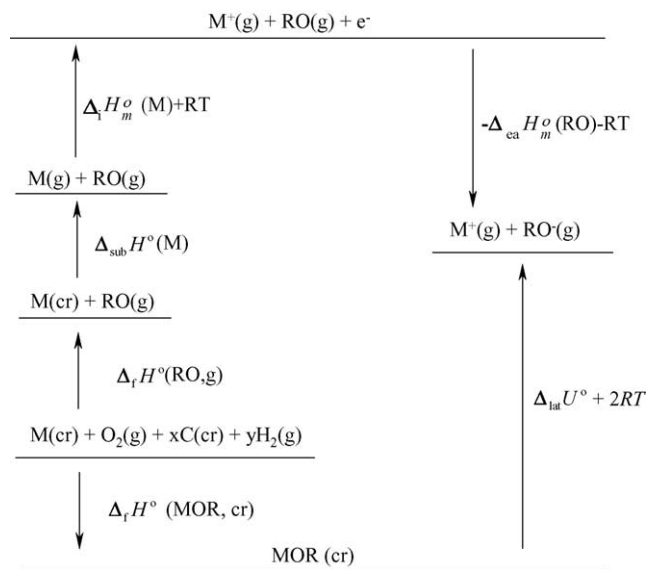
Scheme 2.

Table 3
Reaction enthalpies, and standard enthalpies of formation of 2-methyl, 2,6-dimethyl, 2,4,6-trimethyl and 2,6-terbutyl phenoxides ($T = 298.15$ K)

Metal	$-\Delta_r H(1)$ or $-\Delta_r H(2)$ (kJ mol^{-1})	$\Delta_r H_m^\circ(1)$ or $\Delta_r H_m^\circ(2)$ (kJ mol^{-1})	$-\Delta_f H_m^\circ$ (MOR) (kJ mol^{-1})
Li(OPh)	–	–	382.7 ± 1.4[a]
Li(2-MeOPh)	13.9 ± 0.2	-5.3 ± 0.5	398.4 ± 1.1
Li(2,6-Me$_2$OPh)	21.3 ± 0.4	-13.1 ± 1.3	423.4 ± 1.6
Li(2,4,6-Me$_3$OPh)	20.0 ± 0.6	-11.8 ± 1.3	457.3 ± 7.1
Na(OPh)	–	–	326.4 ± 1.4[a]
Na(2-MeOPh)	30.2 ± 0.6	2.2 ± 0.9	346.6 ± 1.4
Na(2,6-Me$_2$OPh)	21.1 ± 0.8	22.4 ± 1.1	399.6 ± 1.5
Na(2,4,6-Me$_3$OPh)	28.8 ± 1.2	12.6 ± 1.3	422.4 ± 7.1
Na(2,6-t-BuOPh)	56.9 ± 0.7	-13.2 ± 0.9	496.6 ± 7.1
K(OPh)	–	–	333.3 ± 3.1[a]
K(2-MeOPh)	24.0 ± 0.5	24.3 ± 0.6	367.8 ± 1.2
K(2,6-Me$_2$OPh)	30.2 ± 0.9	22.8 ± 1.0	399.1 ± 1.4
Rb(OPh)	–	–	345.3 ± 2.9[a]
Rb(2-MeOPh)	21.0 ± 0.4	31.8 ± 0.6	368.8 ± 1.2
Rb(2,6-Me$_2$OPh)	23.7 ± 0.7	33.8 ± 0.9	403.6 ± 1.3
Cs(OPh)	–	–	349.2 ± 1.4[a]
Cs(2-MeOPh)	10.7 ± 1.2	51.0 ± 1.3	387.0 ± 1.6
Cs(2,6-Me$_2$OPh)	21.6 ± 0.7	44.8 ± 0.9	413.6 ± 1.3

[a] Values taken from ref. [5].

Table 4
Enthalpies of formation and electron affinities for phenoxide radicals and lattice energies for the substituted phenoxides[a]

Phenoxide MOR[a]	$\Delta_f H_m^\circ$ (RO, g) (kJ mol^{-1})[c]	$\Delta_{ea} H_m^\circ$ (OR) (kJ mol^{-1})[d]	$\Delta_{lat} U^\circ$ (MOR) (kJ mol^{-1})
LiOPh	56.9 ± 2.4	228.5 ± 9.1	891.9 ± 9.5[b]
Li(O-2-MePh)	15.7 ± 4.8	218.4 ± 11.6	876.5 ± 12.6
Li(O-2,6-Me$_2$Ph)	-22.8 ± 4.8	208.8 ± 19.3	872.6 ± 19.9
Li(O-2,4,6-Me$_3$Ph)	-46.6 ± 8.5	196.3 ± 19.3	895.2 ± 22.3
NaOPh	56.9 ± 2.4	228.5 ± 9.1	759.2 ± 9.5[b]
Na(O-2-MePh)	15.7 ± 4.8	218.4 ± 11.6	748.3 ± 12.6
Na(O-2,6-Me$_2$Ph)	-22.8 ± 4.8	208.8 ± 19.3	772.4 ± 19.9
Na (O-2,4,6-Me$_3$Ph)	-46.6 ± 8.5	196.3 ± 19.3	783.9 ± 22.3
Na(2,6-t-BuOPh)	-134.7 ± 10.9	243.6 ± 19.3	722.7 ± 23.3
KOPh	56.9 ± 2.4	228.5 ± 9.1	671.0 ± 9.9[b]
K(O-2-MePh)	15.7 ± 4.8	218.4 ± 11.6	674.4 ± 12.6
K(O-2,6-Me$_2$Ph)	-22.8 ± 4.8	208.8 ± 19.3	676.8 ± 19.9
RbOPh	56.9 ± 2.4	228.5 ± 9.1	658.8 ± 9.8[b]
Rb(O-2-MePh)	15.7 ± 4.8	218.4 ± 11.6	651.2 ± 12.6
Rb(O-2,6-Me$_2$Ph)	-22.8 ± 4.8	208.8 ± 19.3	657.1 ± 19.9
CsOPh	56.9 ± 2.4	228.5 ± 9.1	630.6 ± 9.5[b]
Cs(O-2-MePh)	15.7 ± 4.8	218.4 ± 11.6	637.3 ± 12.6
Cs(O-2,6-Me$_2$Ph)	-22.8 ± 4.8	208.8 ± 19.3	635.0 ± 19.9

[a] $\Delta_{sub} H_m^\circ$ (Li) = 159.37 ± 0.08 kJ mol^{-1} [8]; $\Delta_{sub} H_m^\circ$ (Na) = 107.32 ± 0.08 kJ mol^{-1} [8]; $\Delta_{sub} H_m^\circ$ (K) = 89.24 ± 0.08 kJ mol^{-1} [8]; $\Delta_{sub} H_m^\circ$ (Rb) 80.88 ± 0.08 kJ mol^{-1} [8]; $\Delta_{sub} H_m^\circ$ (Cs) 76.065 ± 0.008 kJ mol^{-1} [8], $\Delta_i H_m^\circ$ (Li) = 526.41 [8], $\Delta_i H_m^\circ$ (Na) = 502.04 [8], $\Delta_i H_m^\circ$ (K) = 425.02 [8], $\Delta_i H_m^\circ$ (Rb) = 409.22 [8]; $\Delta_i H_m^\circ$ (Cs) = 381.9 kJ [8].
[b] Recalculated with $\Delta_{ea} H_m^\circ$ (OPh) = 2.304 ± 0.094 eV [5,14].
[c] $\Delta_f H_m^\circ$ (RO, g) = D(RO-H) + $\Delta_f H_m^\circ$ (ROH, g) − $\Delta_f H_m^\circ$ (H); D(2-MePhO-H) = 362.3 ± 4.6 kJ mol^{-1} [15], D(2,6 Me$_2$PhO-H) = 357.3 ± 4.6 kJ mol^{-1} [15], D(2,4,6 Me$_3$PhO-H) = 348.3 ± 4.6 kJ mol^{-1} [15], D(2,6-t-Bu$_2$PhO-H) = 345.3 ± 8.3 kJ mol^{-1} [15]; $\Delta_f H_m^\circ$ (H) = 217.998 ± 0.006 kJ mol^{-1} [15], $\Delta_f H_m^\circ$ (2-MePhOH, g) = −128.6 ± 1.3 kJ mol^{-1} [8], $\Delta_f H_m^\circ$ (2,6-Me$_2$PhOH, g) = −162.1 ± 1.2 kJ mol^{-1} [8]; $\Delta_f H_m^\circ$ (2,4,6-Me$_3$PhOH, g) = −176.9 ± 7.1 kJ mol^{-1} [9]; $\Delta_f H_m^\circ$ (2,6-t-Bu$_2$PhOH, g) = −262 ± 7 kJ mol^{-1} [9].
[d] E_{ea} (2-MePhO$^-$) = 2.20 ± 0.12 eV [14], Estimated values in this work: E_{ea} (2,6-Me$_2$PhO) = 2.09 ± 0.20 eV; E_{ea} (2,4,6-Me$_3$PhO$^-$) = 1.97 ± 0.25 eV; E_{ea} (2,6-t-Bu$_2$PhO$^-$) = 2.46 ± 0.20 eV [17].

of the OR radical [13]. Table 4 gives the $\Delta_{lat} U_{298}^\circ$ (MOR) values obtained in this work for alkali phenoxides.

$$\Delta_{lat} U_{298}^\circ(MOR) = \Delta_f H_m^\circ(MOH, cr) + \Delta_f H_m^\circ(OR, g) \\ + \Delta_{sub} H_m^\circ(M) + \Delta_i H_m^\circ(M) \\ - \Delta_{ea} H_m^\circ(OR) - 2RT \quad (4)$$

Lattice energy values were analysed using the Kapustinskii approximation represented by Eq. (5) [12], which has been used to predict how the lattice energy varies with the size of the constituent ions regardless of structure in the solid state.

$$\Delta_{lat} U_0^\circ(MOR) = 1.079 \times 10^5 \frac{\upsilon Z_+ Z_-}{r_+ + r_-} \quad (5)$$

In this expression $\Delta_{lat} U_0^\circ$ (MOR) is the lattice energy at 0 K in kJ mol^{-1}, υ represents the number of ions in the molecule, Z_+ and Z_- the charges of the cation and the anion and r_+ and r_- the respective ion radii in pm. The r_+ and r_- calculated
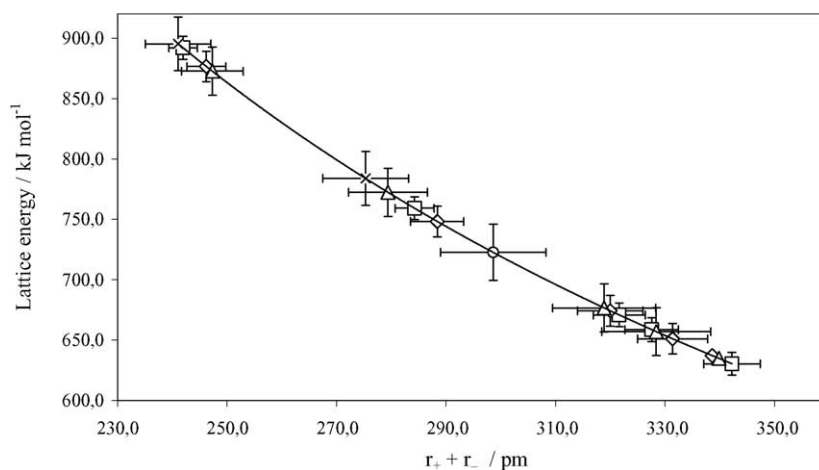

Fig. 1. Lattice energy vs. thermochemical distance [squares: MOPh, diamond: MO(2-MePh), triangle: MO(2,6-Me$_2$Ph), cross: MO(2,4,6-Me$_3$Ph), sphere: MO(2,6-t-Bu$_2$Ph)]. The trend line represents a power function as expected when correlating an energy with a distance (see Eq. (5)).

Table 5
Experimental thermochemical radii (pm) obtained for the phenoxide ions in alkali metal phenoxides[a]

RO^-	LiOR	NaOR	KOR	RbOR	CsOR
PhO^-	151.9 ± 2.8	168.2 ± 3.7	169.6 ± 4.9	161.5 ± 5.0	161.2 ± 5.3
$Ph\text{-}2\text{-}MeO^-$	156.2 ± 3.7	172.4 ± 5.0	168.0 ± 6.1	165.4 ± 6.5	157.6 ± 6.8
$Ph\text{-}2,6\text{-}Me_2O^-$	157.3 ± 5.7	163.4 ± 7.3	166.9 ± 9.4	162.4 ± 10.0	158.8 ± 10.7
$Ph\text{-}2,4,6\text{-}Me_3O^-$	151.1 ± 6.1	159.3 ± 7.9	–	–	–
$Ph\text{-}2,6\text{-}t\text{-}Bu_2O^-$	–	182.6 ± 9.7	–	–	–

[a] r_+ values used in Kapustinskii equation for calculations: $r_+ Li^+ = 90$ pm; $r_+ Na^+ = 116$ pm; $r_+ K^+ = 152$ pm; $r_+ Rb^+ = 166$ pm; $r_+ Cs^+ = 181$ pm [16].

through this procedure are called 'thermochemical radii'. The main importance attached to them lies in their capacity to reproduce the lattice energies when introduced in Eq. (5). As notice by P. Nunes et al. [5] excellent linear correlations had been found for alkali metal alkoxides and phenoxide by plotting d_{M-O} against $(r_+ + r_-)$ allowing the calculation of d_{M-O} in compounds for which no experimental crystallographic data were available, if experimental values exist for some compounds of that family. It was assumed that, to a good aproximation, $\Delta_{lat}U_0^\circ(MOR) = \Delta_{lat}U_{298}^\circ(MOR)$ [5] and so, from data presented in Table 4 it was possible to derive the M–OR interatomic distances $(r_+ + r_-)$. Fig. 1 shows that, as expected, experimental lattice energies correlate clearly with the interatomic distances $(r_+ + r_-)$. Thermochemical radii of

the phenoxide anions (r_-) could be determined using the radii of the metallic cations given by Shannon [16]. Table 5 gives the thermochemical radii experimentally obtained for the alkali phenoxides in this study.

To estimate lattice energies for unmeasured phenoxides, $\Delta_{lat}U_{298}^\circ$, and from it the standard molar enthalpies of formation, the following procedure was applied. The experimental lattice energies were compared with the estimated lattice energies considering as first approximation the average experimental r_- values taken from Table 5 and r_+ values taken from Shannon [16]. Using solver of MS Excel 7.0, the difference between them was minimized by least square regression taking as variables the r_- and the r_+ values. The new thermochemical radii values were used to estimate a new set of data

Table 6
Lattice energies and enthalpies of formation of alkali metal phenoxides

Phenoxide	$\Delta_{lat}U^\circ$ (MOR) (kJ mol^{-1})		$-\Delta_f H_m^\circ$(MOR) (kJ mol^{-1})	
	Experimental[a]	Estimated[b]	Experimental[c]	Estimated[d]
LiOPh	891.9 ± 9.5[e]	884.0	382.7 ± 1.4[e]	374.8
Li(O-2-MePh)	876.5 ± 12.6	875.0	398.4 ± 1.1	396.9
Li(O-2,6-Me$_2$Ph)	872.6 ± 19.9	882.1	423.4 ± 1.6	432.9
Li(O-2,4,6-Me$_3$Ph)	895.2 ± 22.3	912.6	457.3 ± 7.1	474.6
Li(O-2,6-t-Bu$_2$Ph)	–	830.7	–	528.2
NaOPh	759.2 ± 9.5[e]	762.7	326.4 ± 1.4[e]	329.9
Na(O-2-MePh)	748.3 ± 12.6	756.0	346.6 ± 1.4	354.3
Na(O-2,6-Me$_2$Ph)	772.4 ± 19.9	761.3	399.6 ± 1.5	388.5
Na (O-2,4,6-Me$_3$Ph)	783.9 ± 22.3	783.9	422.4 ± 7.1	422.4
Na(2,6-t-BuOPh)	722.7 ± 23.3	722.7	496.6 ± 7.1	496.6
KOPh	671.0 ± 9.9[e]	676.2	333.3 ± 3.1[e]	338.5
K(O-2-MePh)	674.4 ± 12.6	670.9	367.8 ± 1.2	364.3
K(O-2,6-Me$_2$Ph)	676.8 ± 19.9	675.1	399.1 ± 1.4	397.4
K(O-2,4,6-Me$_3$Ph)	–	692.8	–	426.4
K(O-2,6-t-Bu$_2$Ph)	–	644.6	–	513.5
RbOPh	658.8 ± 9.8[e]	657.8	345.3 ± 2.9[e]	344.2
Rb(O-2-MePh)	651.2 ± 12.6	652.8	368.8 ± 1.2	370.3
Rb(O-2,6-Me$_2$Ph)	657.1 ± 19.9	656.7	403.6 ± 1.3	403.2
Rb(O-2,4,6-Me$_3$Ph)	–	673.4	–	431.2
Rb(O-2,6-t-Bu$_2$Ph)	–	627.8	–	520.9
CsOPh	630.6 ± 9.5[e]	636.2	349.2 ± 1.4[e]	354.8
Cs(O-2-MePh)	637.3 ± 12.6	631.5	387.0 ± 1.6	381.2
Cs(O-2,6-Me$_2$Ph)	635.0 ± 19.9	635.2	413.6 ± 1.3	413.8
Cs(O-2,4,6-Me$_3$Ph)	–	650.8	–	440.7
Cs(O-2,6-t-Bu$_2$Ph)	–	606.1	–	533.4

[a] Experimental values calculated from Eq. (4).
[b] Estimated values using optimized r_+ and r_- values: $r_+(Li^+) = 83.0$ pm; $r_+(Na^+) = 121.8$ pm; $r_+(K^+) = 158.0$ pm; $r_+(Rb^+) = 166.9$ pm; $r_+(Cs^+) = 178.1$ pm; $r_-(OPh) = 161.1$ pm; $r_-(O\text{-}2\text{-}MePh) = 163.7$ pm; $r_-(O\text{-}2,6\text{-}Me_2Ph) = 161.7$ pm; $r_-(O\text{-}2,4,6\text{-}Me_3Ph) = 153.5$ pm; $r_-(O\text{-}2,6\text{-}t\text{-}Bu_2Ph) = 176.8$ pm.
[c] Experimental values calculated from Eqs. (1) and (2).
[d] Estimated values obtained using Scheme 2 and estimated lattice energy values.
[e] Experimental values [5] used to recalculate lattice energies with E_{ea} (PhO) $= 2.30 \pm 0.09$ eV [14].

and through Scheme 2 to calculate the enthalpies of formation of some unknown alkali metal phenoxides as well as recalculate the enthalpies of formation of measured phenoxides with optimized r_+ and r_- values. Table 6 shows the comparison between experimental and estimated lattice energy and standard molar enthalpies of formation for the compounds under study. The new set of r_+ and r_- values is consistent as it reproduces the experimental $\Delta_{lat}U^\circ_{298}$ (MOR) data with an average absolute deviation of 4.4 kJ mol^{-1} and a maximum relative deviation of 1.5%. These values were subsequently used to estimate the enthalpies of formation of various MOR compounds using Eq. (4) when no experimental values exist.

Results obtained suggest that no steric effects exist by the presence of one, two or three methyl groups in positions 2, 2 and 6, or 2, 4 and 6 of the phenol ring. Only the terbutyl groups in positions 2 and 6 reveals a different thermochemical radii value as seen from Table 5 and thus if steric effects exist in this family of compounds it will be only in the 2,6-diterbutylphenoxides.

Acknowledgments

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