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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: $\Delta_f H^\circ_m$ (MOR, cr)/kJ mol^{-1} = −398.4 ± 1.1 (LiO-2-MePh), −423.4 ± 1.6 (LiO-2,6-Me_2Ph), −457.3 ± 7.1 (LiO-2,4,6-Me_3Ph), −346.6 ± 1.4 (NaO-2-MePh), −399.1 ± 1.5 (NaO-2,6-Me_2Ph), −422.4 ± 7.1 (NaO-2,4,6-Me_3Ph), −496.6 ± 7.1(NaO-2,6-*t*-Bu_2Ph), −367.8 ± 1.2 (KO-2-MePh), −399.1 ± 1.4 (KO-2,6-Me_2Ph), −368.8 ± 1.2 (RbO-2-MePh), −403.6 ± 1.3 (RbO-2,6-Me_2Ph), −387.0 ± 1.6 (CsO-2-MePh) and −413.6 ± 1.3 (CsO-2,6-Me_2Ph). 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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Keywords: Thermochemistry; Alkali metals; Enthalpy of formation; Phenoxides; Lattice energy

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_2O_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, ν 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, ν 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, ν 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, ν 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, ν 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, ν 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, ν 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, ν 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, ν 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, ν 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, ν 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, ν 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, ν 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, ν cm^{-1}): 1574 (s), 1543 (w), 1459 (vs), 1411 (vs), 1375 (vs), 1356 (vs), 1291

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