Standard Molar Enthalpies of Formation of Mg and Ca Alkoxides

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The enthalpies of formation of some alkaline-earth alkoxides were determined by reaction-solution calorimetry ($\Delta_f H^o$[Mg(OMe)$_2$] = –792.6±1.2 kJ/mol; $\Delta_f H^o$[Mg(OEt)$_2$] = –847.9±2.7 kJ/mol; $\Delta_f H^o$[Ca(OMe)$_2$] = –890.8±6.4 kJ/mol; $\Delta_f H^o$[Ca(OEt)$_2$] = –924.5±2.6 kJ/mol; $\Delta_f H^o$[Ca(OBu)$_2$] = –989.8±5.4 kJ/mol) and allowed us to extend a previously developed model for predicting the enthalpies of formation of Be, Sr and Ba alkoxides.

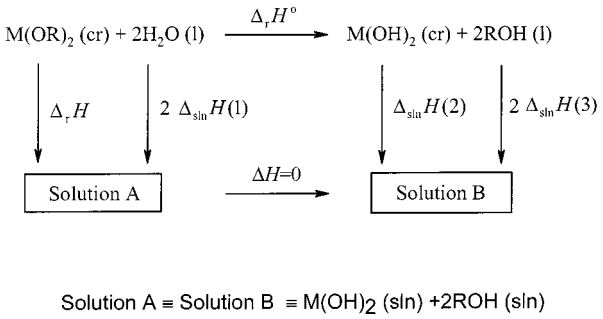
Introduction

Alkaline and alkaline-earth metal alkoxide compounds are of major importance in synthetic chemistry.[1] However, thermochemical data for these substances is rather scarce. Previous results obtained for sodium and lithium alkoxides[2,3] show that there exists a linear relation between the enthalpies of formation of the alkoxides and those of the corresponding alcohols for short-chain unbranched alkoxides. A model based on the alkoxide energy calculations and a simple electrostatic model was also developed, which enabled us to predict unknown alkali metal alkoxide enthalpies of formation.

In this paper we extend the previously developed model to alkaline-earth alkoxides and use it for the prediction of some unmeasured Be, Sr and Ba alkoxides.

Results and Discussion

The enthalpies of formation of magnesium and calcium alkoxides were calculated according to Scheme 1 (reaction with water, used for all the compounds studied in this paper) or Scheme 2 [reaction with 0.1 M HCl, used for Ca(OEt)$_2$]. In these schemes, $\Delta_r H^o$ represents the reaction enthalpy with all the compounds in their standard state, $\Delta_r H$ the experimentally measured reaction enthalpy, $\Delta_{sln} H(2)$ the dissolution enthalpy for stoichiometric amounts of M(OH)$_2$ in H_2O, $\Delta_{sln} H(3)$ the dissolution enthalpy of the alcohol in H_2O + M(OH)$_2$, $\Delta_{sln} H(5)$ the dissolution of $CaCl_2$ in 0.1 M HCl, $\Delta_{sln} H(6)$ the dissolution of ethanol in a 0.1 M HCl + $CaCl_2$ solution, and $\Delta_{sln} H(7)$ the dissolution of water in 0.1 M HCl solution. $\Delta_{sln} H(1)$ (dissolution of water in water) and $\Delta_{sln} H(4)$ (dissolution of 0.1 M HCl in 0.1 M HCl) are obviously zero.



Scheme 1. Reaction with water

As the concentrations of M(OH)$_2$ in solution were always very small [about 1 mol M(OH)$_2$ in 4 × 10^5 mol water] an infinite dilution can be assumed and $\Delta_{sln} H(2)$ can be calculated as –2.30 kJ/mol for magnesium hydroxide and –16.73 kJ/mol for the calcium analogue using the data in Table 1.[4,5] In the cases of ethanol and methanol, $\Delta_{sln} H(3)$ values were calculated from the differences between the enthalpies of formation of the pure alcohols and the respective enthalpies of formation at infinite dilution in water (Table 2 and Equation 1 and 2). $\Delta_{sln} H(3)$ for butanol was taken as −7.39 ± 0.59 kJ/mol.[3]

$$\Delta_{sln} H(3)\ (MeOH) = \Delta_f H^o\ (CH_3OH,\infty\ H_2O) - \Delta_f H^o\ (CH_3OH,l) = -7.3 \pm 0.4\ kJ/mol \quad (1)$$

$$\Delta_{sln} H(3)\ (EtOH) = \Delta_f H^o\ (C_2H_5OH,\infty\ H_2O) - \Delta_f H^o\ (C_2H_5OH,\ l) = -10.7 \pm 0.6\ kJ/mol \quad (2)$$

The fact that the above $\Delta_{sln} H(3)$ values were obtained in water and not in H_2O + M(OH)$_2$ solutions should not be relevant due to the low concentrations of M(OH)$_2$ in solution. This is in keeping with the values in a previous publication[3] where the dissolution of butanol in water, H_2O + LiOH and H_2O + NaOH was measured, and showed no difference within experimental error.

The enthalpies of formation of aqueous 0.1 M HCl and crystalline calcium chloride are known (Table 1). The dissolution of calcium chloride in 0.1 M HCl and of ethanol in $CaCl_2$ + 0.1 M HCl solution was measured (Table 2). The dissolution of water in the solvent is negligible (smaller than the detection limit of the apparatus) and even when multiplied by 1104 yields a minor contribution to the final $\Delta_r H^o$ value (smaller than the experimental error). Therefore, $\Delta_{sln} H(7)$ was neglected.

Schemes 1 and 2 lead to Equations 3 and 4, that allow the calculation of the enthalpies of formation of the metal alkoxides shown in Table 3.

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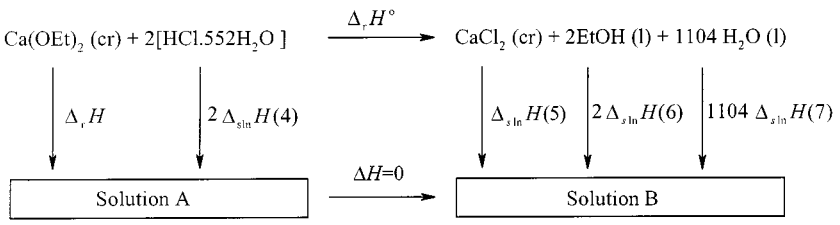


Solution A ≡ Solution B ≡ $CaCl_2$ (sln) +2EtOH (sln) + n ($HCl \cdot 552H_2O$)

Scheme 2. Reaction with 0.1 M HCl

Table 1. Auxiliary data (T = 298.15 K)

Compound	$\Delta_f H^o$ (kJ/mol)	Ref.
H_2O, l	–285.830	4
CH_3OH, l	–239.1±0.3	5
$CH_3OH \cdot \infty H_2O$	–246.4±0.3	5
C_2H_5OH, l	–277.5±0.4	5
$C_2H_5OH \cdot \infty H_2O$	–288.2±0.4	5
C_4H_9OH, l	–327.3±0.4	5
$Mg(OH)_2$, cr	–924.54	4
$Mg(OH)_2$, ai	–926.84	4
Mg, g	147.70	4
$Ca(OH)_2$, cr	–986.09	4
$Ca(OH)_2$, ai	–1002.82	4
Ca, g	178.2	4
$CaCl_2$, cr	–795.8	4
$HCl \cdot 552\ H_2O$	–166.596	4

Table 2. Dissolution enthalpies (T = 298.15 K)

Compound	$\Delta_{sln}H(3)$ (kJ/mol)[a]	$\Delta_{sln}H(6)$ (kJ/mol)[b]	$\Delta_{sln}H(5)$ (kJ/mol)[c]
CH_3OH	–7.3±0.4[d]	–	–
C_2H_5OH	–10.7±0.6[d]	–9.4±1.6	–
C_4H_9OH	–7.39±0.59[e]	–	–
$CaCl_2$	–	–	–81.8±1.1

[a] Dissolution in water. – [b] Dissolution in 0.1 M HCl + $CaCl_2$. – [c] Dissolution in 0.1 M HCl. – [d] Calculated from data in Table 1. – [e] Measured in ref.[3]

Table 3. Reaction enthalpies, and standard enthalpies of formation of magnesium and calcium alkoxides (T = 298.15 K).

Alkoxide	$\Delta_r H$[a] (kJ/mol)	$\Delta_f H^o$[$M(OR)_2$,cr] (kJ/mol)	$\Delta_r H^o$[a] (kJ/mol)
$Mg(OMe)_2$	–55.4±0.7	–792.6±1.2	–38.5±1.1
$Mg(OEt)_2$	–83.7±2.3	–847.9±2.7	–60.0±2.6
$Ca(OMe)_2$	–33.2±6.3	–890.8±6.4	–1.9±6.4
$Ca(OEt)_2$	–83.1±2.2	–924.5±2.6	–45.0±2.5
–	–192.1±9.1[b]	–926.1±9.7	–
$Ca(OBu)_2$	–110.7±5.2	–989.8±5.4	–79.2±5.3

[a] Reaction with water unless stated otherwise. – [b] Reaction with 0.1 M HCl.

$$\Delta_f H^o [M(OR)_2] = \Delta_f H^o [M(OH)_2,cr] + 2\Delta_f H^o [ROH, l] - 2\Delta_f H^o [H_2O, l] - \Delta_r H + \Delta_{sln} H(2) + 2\Delta_{sln} H(3) \quad (3)$$

$$\Delta_f H^o [Ca(OEt)_2, cr] = \Delta_f H^o [CaCl_2,cr] + 2\Delta_f H^o [EtOH, 1] - 2\Delta_f H^o [HCl \cdot 552H_2O] - \Delta_r H + \Delta_{sln} H(5) + 2\Delta_{sln} H(6) + 1104\ \Delta_{sln} H(7) \quad (4)$$

As a first comment we note the good agreement between the values for the enthalpy of formation of $Ca(OEt)_2$ obtained by the two different methods referred to above. Since the reaction with HCl was studied mainly to test the consistency of the results, in all subsequent calculations the values derived from the reactions with water will be used.

A plot of the enthalpies of formation of the crystalline alkoxides against the enthalpies of formation of the corresponding alcohols in their standard reference states is shown in Figure 1. This type of plot has been used before for many compound families,[6] including sodium[2] and lithium alkoxides,[3] and it is useful to assess the reliability of the data. For calcium alkoxides, and using the three points for R = Me, Et and Bu, a fairly linear correlation (r = 0.9922; uncertainty intervals are standard deviations) (Equation 5) is obtained. The slope defined by the two points for Mg alkoxides (R = Me and Et) is 1.44.

$$\Delta_f H^o (Ca(OR)_2) = (1.13 \pm 0.14)\ \Delta_f H^o (ROH, l) - (617 \pm 39) \quad (5)$$

To understand the plot of Figure 1 (or Equation 5) we can use Equation 6, where $\Delta_r H^o$ is simply defined in terms of the standard enthalpies of formation of reactants and products. If a linear correlation between $\Delta_f H^o$ [$M(OR)_2$,cr] and $\Delta_f H^o$ (ROH,l) is observed, this means that $\Delta_r H^o$ is constant for several R. On the other hand, as evidenced by Equation 6, the slope of the line should be close to 2 (the number of alkoxide ligands bound to M). However, this is not observed either for Mg or Ca compounds, nor is $\Delta_r H^o$ constant (Table 3) in Equation 5. Similar behaviour had been noticed for some K, Rb and Cs alkoxides.[7] This type of plot should work well only if the crystal structure has little effect on the energetics. Since none of the crystal structures are known, and since changing the anions and/or the cations is very likely to change the crystal structure, Figure 1 should be used mainly as a visual aid to find trends in the values.

$$\Delta_f H^o [M(OR)_2, cr] = 2\Delta_f H^o [ROH, l] + \Delta_f H^o [M(OH)_2, cr] - 2\Delta_f H^o [H_2O, l] - \Delta_r H^o \quad (6)$$

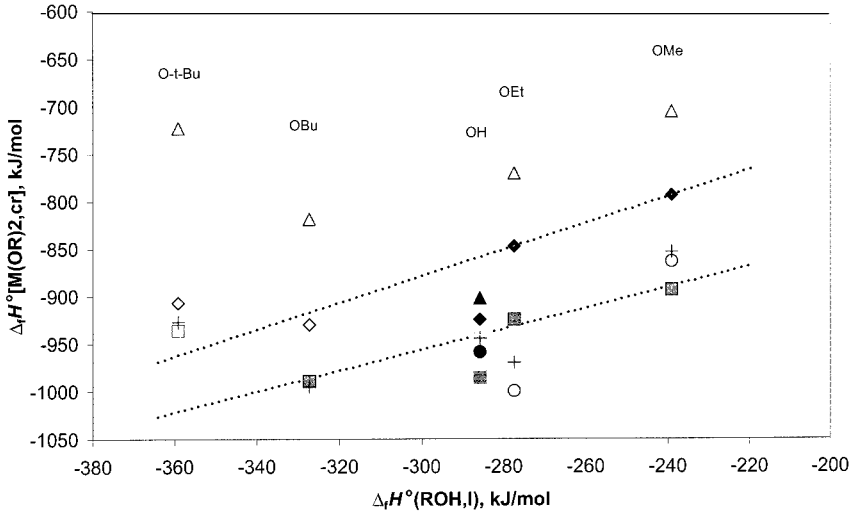
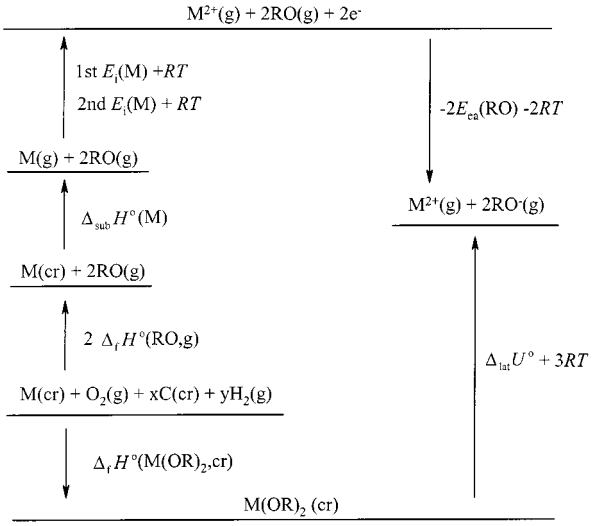


Figure 1. Enthalpies of formation of alkaline-earth metal alkoxides versus the enthalpies of formation of the corresponding alcohols (experimental data: filled symbols; estimated data: empty symbols; Be: triangle; Mg: diamond; Ca: square; Sr: circle; Ba: cross); the lower line is a linear regression using the three experimental values for Ca, and the upper line is simply a line passing through the two experimental Mg values, which are included mainly as a visual guide

Table 4. Lattice energies of magnesium and calcium alkoxides

Alkoxide $M(OR)_2$[a]	$\Delta_f H°(RO_2,g)$ (kJ/mol)[c]	EA(OR) (kJ/mol)[d]	$\Delta_{lat}U°[M(OR)_2]$ (kJ/mol)
$Mg(OH)_2$[b]	39±4	176.4±1.0	2990.8±8.2
$Mg(OMe)_2$	18±4	151.4±2.1	2866.9±9.1
$Mg(OEt)_2$	–17±4	166.5±3.2	2822±10
$Ca(OH)_2$[b]	39±4	176.4±1.0	2629.8±8.2
$Ca(OMe)_2$	18±4	151.4±2.1	2542±11
$Ca(OEt)_2$	–17±4	166.5±3.2	2476±10
$Ca(OBu)_2$	–63±4	171±14	2440±30

[a] $\Delta_{sub}H°$(Mg) = 147.70 kJ/mol,[4] $\Delta_{sub}H°$(Ca) = 178.2 kJ/mol,[4] 1st E_i (Mg) = 743.935,[4] 2nd E_i (Mg) = 1456.869,[4]1st E_i (Ca) = 596.05,[4] 2nd E_i (Ca) = 1151.65.[4] – [b] $\Delta_f H°[M(OH)_2]$ taken from Table 1. – [c] Taken from D. F. McMillen, D. M. Golden, *Ann. Rev. Phys. Chem.* **1982**, *33*, 493. – [d] Taken from S. G. Lias, J. E. Bartmess, J. F. Liebman, J. L. Holmes, R. D. Levin, W. G. Mallard, *J. Phys. Chem.*, **1988**, *17*, Suppl. no. 1.



Scheme 3

Another way of discussing the data in Table 4 involves the calculation of lattice energies ($\Delta_{lat}U°$) of magnesium and calcium alkoxides.

These values, displayed in Table 4, were obtained from the standard enthalpies of formation of the alkoxides and from literature data, according to Scheme 3. The high ionic character of the alkoxides is indicated by their lattice energies, which are under 200 kJ/mol lower than the lattice energies of the corresponding hydroxides.

Let us assume a simple ionic model and the Kapustinskii approximation represented by Equation 7.[8] In this expression, v represents the number of ions in the molecule, Z_+ and Z_- the charges of the cation and anion and r_+ and r_- the respective radii in pm. As the ionic radii of Mg^{2+} and Ca^{2+} are known,[9] the ionic radii of the alkoxide anions can be derived from the data in Table 4. The results are shown in Table 5, which also includes early data for alkaline-earth and alkali metal alkoxides [2,3,7] and estimates of the radii of the alkoxide ions in some alkaline-earth metal alkoxides not studied in this work.

$$\Delta_{lat}U° = \frac{1.079\times10^5 . v . Z_+ Z_-}{r_+ + r_-} \quad (7)$$

The radii calculated by the above procedure are called "thermochemical radii" and have no special physical meaning, apart from reproducing lattice energies when introduced in Equation 7. It is to be noted that the values of the *n*-butoxy anion always have a greater error than the others. This is mainly due to the huge error in the electroaffinity of the butoxy ion.

Using these estimated radii and Scheme 3, it is possible to calculate the enthalpies of formation for some unknown alkaline-earth metal alkoxides (Table 6). The error bars are

Table 5. Thermochemical radii[a] calculated or estimated[b] for the alkoxide ions in alkali and alkaline-earth metal alkoxides[c]

RO^-	$Be(OR)_2$	LiOR[e]	$Mg(OR)_2$	NaOR[f]	$Ca(OR)_2$	KOR[g]	$Sr(OR)_2$	RbOR[g]	$Ba(OR)_2$	CsOR[g]
HO^-	120.2±1.1[d]	119.8±1.3	130.5±1.2	127.4±1.5	132.2±1.3	121±3	130.4±1.3[d]	118±3	129.7±1.4[d]	116±3
MeO^-	(130±2)	130.1±1.5	**139.8±1.2**	141.8±1.9	**140.6±1.5**	138±4	(140±6)	131±4	(140±6)	131±4
EtO^-	(132±2)	132.4±1.6	**143.4±1.3**	145.2±2.0	**147.5±1.5**	134±4	(136±6)	127±3	(138±6)	129±4
$nBuO^-$	(135±4)	135.0±3.6	(145±5)	144.9±4.8	**151.3±3.4**	144±10			(148±12)	139±10
$tBuO^-$	(146±3)	146.1±2.1	(154±3)	154.2±3.0	(167±8)	160±6			(170±8)	160±6

[a] Thermochemical radii studied in the present paper are in bold. – [b] Estimated thermochemical radii in parentheses[c] $r_+(Li^+)$ = 90 ±1 pm, $r_+(Na^+)$ = 116 ±1 pm, $r_+(K^+)$ = 152 ±1 pm, $r_+(Rb^+)$ = 166 ±1 pm, $r_+(Cs^+)$ = 181 ±1 pm, $r_+(Be^{2+})$ = 59 ±1 pm, $r_+(Mg^{2+})$ = 86 ±1 pm, $r_+(Ca^{2+})$ = 114 ±1 pm, $r_+(Sr^{2+})$ = 132±1 pm, $r_+(Ba^{2+})$ = 149±1 pm.[9] – [d] Δ_fH^o[$Be(OH)_2$,cr] = –902.5 kJ/mol, Δ_fH^o[$Sr(OH)_2$,cr] = –959.0 kJ/mol, Δ_fH^o[$Ba(OH)_2$,cr] = –944.7 kJ/mol, $\Delta_fH^o(Be^{2+},g)$ = 2993.23 kJ/mol, $\Delta_fH^o(Sr^{2+},g)$ = 1790.54 kJ/mol, $\Delta_fH^o(Ba^{2+},g)$ = 1660.38 kJ/mol.[4] – [e] Calculated from data in ref.[3] – [f] Calculated from data in ref.[2] – [g] From ref.[7]

large (50 kJ/mol excluding the butoxides and 90 kJ/mol for the butoxides) when compared with those for the alkoxides measured on this paper (2–6 kJ/mol). The main reason is that a small error in the radii will be amplified in the lattice energy values (since $\Delta_{lat}U^o$ is a big value) and therefore in the values of the enthalpy of formation.

Table 6. Lattice energies and enthalpies of formation of alkaline–earth alkoxides; estimated values in parentheses

Alkoxide	$\Delta_{lat}U^o$ kJ/mol	Δ_fH^o[$M(OR)_2$] kJ/mol
$Be(OMe)_2$	(3425±40)	(–706±41)
$Be(OEt)_2$	(3390±40)	(–771±41)
$Be(OBu)_2$	(3337±71)	(–819±77)
$Be(OtBu)_2$[a]	(3158±49)	(–723±51)
$Mg(OMe)_2$	2866.9±9.1	–792.6±1.2
$Mg(OEt)_2$	2822±10	–847.9±2.7
$Mg(OBu)_2$	(2803±62)	(–930±68)
$Mg(OtBu)_2$[a]	(2698±36)	(–907±39)
$Ca(OMe)_2$	2542±11	–890.8±6.4
$Ca(OEt)_2$	2476±10	–924.5±2.6
$Ca(OBu)_2$	2440±30	–989.8±5.4
$Ca(OtBu)_2$[a]	(2304±66)	(–936±68)
$Sr(OMe)_2$	(2380±53)	(–864±54)
$Sr(OEt)_2$	(2416±55)	(–1000±56)
$Sr(OBu)_2$	–	–
$Sr(OtBu)_2$[a]	–	–
$Ba(OMe)_2$	(2240±47)	(–854±48)
$Ba(OEt)_2$	(2256±48)	(–970±49)
$Ba(OBu)_2$	(2180±88)	(–995±93)
$Ba(OtBu)_2$[a]	(2029±51)	(–927±53)

[a] $\Delta_fH^o(OtBu)$ = –91±5 kJ/mol from D. F. McMillen, D. M. Golden, *Ann. Rev. Phys. Chem.* **1982**, *33*, 493; $E_{ea}(OtBu)$ = 184.4±5.2 from S. G. Lias, J. E. Bartmess, J. F. Liebman, J. L. Holmes, R. D. Levin, W. G. Mallard, *J. Phys. Chem.* **1988**, *17*, Suppl. no. 1.

Nevertheless, if no other values exist, those can be quite useful. In the future we intend to extend this study to other alkaline-earth metal alkoxides to achieve better data for these compounds.

Knowing the structures would give deep insight into in these kinds of compounds. Despite all efforts, it has not yet been possible to obtain single crystals, and powder studies have yet to be undertaken.

Experimental Section

Materials: Methanol (Merck, 99.8%) and ethanol (Merck, 99.8%) were pre-dried over calcium sulfate, refluxed over activated magnesium and iodine, and finally distilled. Butanol (Sigma, 99.0%) was dried over calcium hydride and distilled. Magnesium (turnings, Sigma) and calcium (granules, Sigma) were used as supplied and stored in an oxygen- and water-free glovebox. Iodine was sublimed twice before use. Pentane was distilled over P_2O_5 and stored in the glovebox over 4 Å molecular sieves.

Physical Measurements: Infrared spectra were determined using a Perkin–Elmer 577 spectrophotometer with samples mounted as Nujol mulls between KBr plates. Elemental analyses were performed on a Perkin–Elmer 240 C (C, H) automatic analyzer or by gravimetric analyses (Mg as magnesium oxide,[10] Ca as calcium oxalate[11]). Iodine was qualitatively analyzed by an energy-dispersive X-ray spectrometer with a primary photon beam produced by a high power rhodium anode X-ray tube (Kevex Delta XRF Analyst System).

Alkoxide Syntheses: The studied alkoxides are moisture sensitive. Therefore, all syntheses were performed inside an oxygen- and water-free (<5 ppm) glovebox. Alcohols were degassed before use. Magnesium alkoxides were prepared by addition of the metal to an excess of alcohol (methanol or ethanol) containing a small amount of sublimed iodine (acting as a catalyst) and stirred for several days inside the glovebox at room temperature. The solution was taken to dryness, washed twice with pentane and dried under high vacuum (10^{-4}–10^{-5} Torr). The calcium alkoxides (methoxy, ethoxy and butoxy) were synthesized in a similar way without adding the catalyst. One of the problems that may occur is the formation of metal hydroxides due to the presence of water, and which are virtually impossible to separate from the alkoxides. Another problem is ensuring that the alkoxides are completely dry, i.e. all the excess alcohol must be removed. IR spectra showed that all the alkoxides used in

Table 7. Elemental analysis of magnesium and calcium alkoxides

Alkoxide	Found %C	%H	%M	Theoretical %C	%H	%M
$Mg(OMe)_2$	27.95	6.77	–	27.90	7.03	–
$Mg(OEt)_2$	39.83	8.51	21.1	41.99	8.81	21.24
$Ca(OMe)_2$	23.21	5.97	–	23.52	5.92	–
$Ca(OEt)_2$	38.23	7.82	31.0	36.90	7.74	30.78
$Ca(OBu)_2$	51.03	9.65	–	51.57	9.74	–

this work were alcohol- and hydroxide-free. Elemental analysis of the alkoxides (C, H, metal) was also performed (metal analysis on only some of them) to assess the purity (Table 7). For the magnesium compounds energy-dispersive X-ray spectrometry was conducted to check if any iodine was incorporated, the result always being negative.

Reaction-Solution Calorimetry: The calorimeter used was specially built for the study of oxygen- and water-sensitive compounds, and the experimental procedure was described in a previous paper.[2] 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. To determine the enthalpies of formation of the alkoxides, their reactions with water were studied in the calorimeter. As a test for consistency, the reaction of $Ca(OEt)_2$ with a 0.1 M aqueous solution of HCl was also studied.

Acknowledgments

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