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Standard enthalpies of formation of sodium alkoxides

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Abstract

The standard enthalpies of formation of several crystalline sodium alkoxides, ΔH_f^0(NaOR, cr), have been determined by reaction-solution calorimetry. A linear correlation has been found between ΔH_f^0(NaOR, cr) and ΔH_f^0(ROH, 1/cr) for R = n-alkyl, enabling the prediction of data for other sodium alkoxides. The results were also used to derive the lattice energies and the thermochemical radii of the anions OR^-.

Introduction

Despite the use of alkaline metal alkoxides in chemical syntheses [1], there are almost no thermochemical data for this family of compounds. The present paper describes reaction-solution calorimetry studies that have given the standard enthalpies of formation of several crystalline sodium alkoxides. These data were derived from reactions 1 and 2, which proved to be fast, quantitative, and quite exothermic.

$$\mathrm{NaOR(cr)} + \mathrm{H_2O(l)} \longrightarrow \mathrm{NaOH(sln)} + \mathrm{ROH(sln)} \quad (1)$$

$$\mathrm{NaOR(cr)} + \mathrm{HCl(aq)} \longrightarrow \mathrm{NaCl(sln)} + \mathrm{ROH(sln)} \quad (2)$$

Experimental

Materials. Tetrahydrofuran was pre-dried over Linde 4 Å molecular sieves and distilled from sodium, potassium, and benzophenone. Pentane was dried over P_2O_5, distilled, and kept over Linde 4 Å molecular sieves. Toluene-d_8 was dried over sodium and distilled. Methanol and ethanol were refluxed over activated magnesium and iodine and distilled [2]. Isopropanol, butanol, and t-butanol were dried over calcium hydride and distilled. 2-Pentanol was refluxed over CaO, distilled, refluxed over magnesium, and fractionally distilled. Phenol was purified by sublimation.

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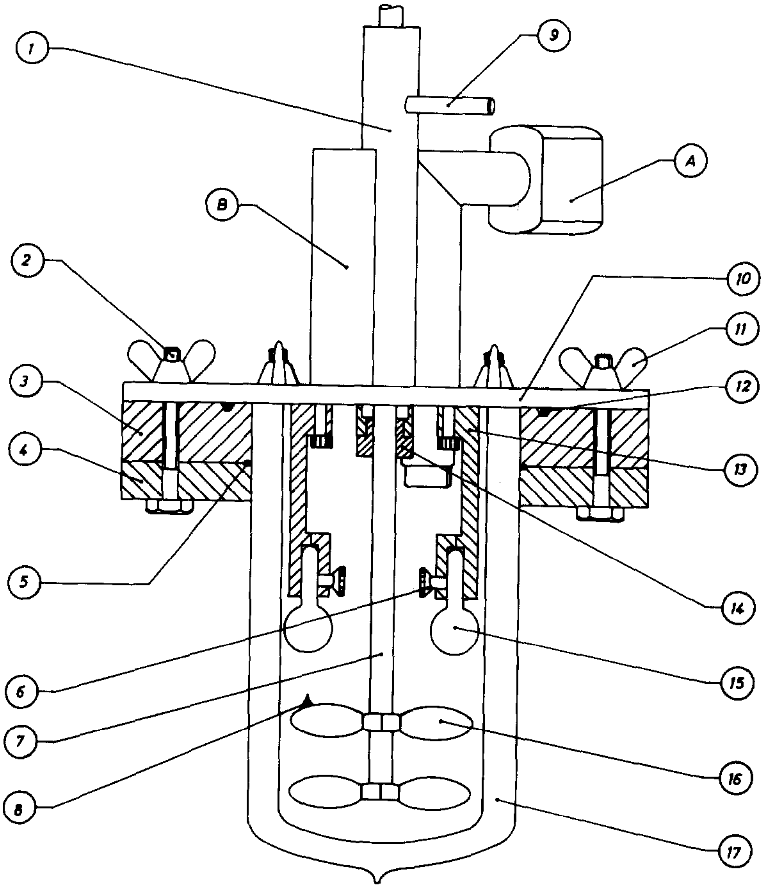

Fig. 1. Calorimetric vessel. See text for description.

Physical measurements. Infrared spectra were obtained with a Perkin-Elmer 577 spectrophotometer with samples mounted as Nujol mulls between KBr plates. ^{1}H NMR spectra were recorded with a Bruker SY80 FT spectrometer and are referenced to TMS. Elemental analyses were obtained with a Perkin-Elmer automatic analyser.

Sodium alkoxides syntheses. Sodium alkoxides are moisture sensitive and so all syntheses and subsequent manipulations were conducted under an inert atmosphere. Solvents were degased before use. All syntheses were carried in a similar way. The alcohol was stirred with an excess of sodium in THF for several hours. The residual sodium was removed and the solution evaporated to dryness. The presence of water in the reaction media would lead to the formation of NaOH, which is very difficult to separate from the alkoxide and a slight contamination by NaOH might significantly affect the calorimetric results. Sodium alkoxides were characterized by IR spectroscopy, elemental analyses, and ^{1}H NMR.

Calorimeter. The calorimeter used (Fig. 1) was specially built for the study of compounds hyper-sensitive to air and moisture. Its design was based on earlier models [3], but several modifications were introduced. The reaction vessel (17) was a 150 ml Dewar flask with two acrylic flanges (3 and 4) and a brass lid (10). This set-up was held together by six brass screws (2), two of which were used to hold the vessel in the thermostat bath. Attached to the brass lid· were four polypropylene ampoule holders (13) with screws (6), two glass tubes (one for the thermometer probe, **B**, and the other for the calibrating resistance, A), and the stirring system. Constant stirring was obtained by using an SPN precision agitator.

The stainless-steel stirring shaft (7) was held in place by two Teflon bearings (14) contained inside a copper tube (1). This system allowed nearly frictionless stirring while remaining nearly gas tight. As an additional precaution, the copper tube was flushed with argon (9) during the calorimetric runs. The stirring system served also to permit breaking of the ampoules (15) by raising the stirring shaft. A gear allowed this operation without stopping the stirrer engine. This gear was controlled by a lever, so that the calorimeter shaft could be moved up and down. An important detail of the calorimeter head was that all the metallic parts in contact with the solution were covered with a layer of an inert polymer.

In a typical experiment, 12 mm diameter glass ampoules were loaded with 10–200 mg of compound, sealed under vacuum and weighed to $\pm 10^{-5}$ g with a Mettler H54AR balance. A mass correction for vacuum was made. These ampoules were then placed in the holders, the vessel filled with 140 ml of the appropriate reaction mixture, and immersed in a water bath maintained at 25 ° C (±0.001° C) by a Tronac PTC 40 Precision Temperature Controller. After thermal equilibration, an electrical calibration was made with a low temperature coefficient resistance of ca. 47 Ω, placed inside a glass tube filled with silicone oil. The power came from a Delta Elektronika EO30-3 power supply. The voltage across the heater was measured with a Keithley 191 voltmeter and the current was determined from the voltage decrease across a 1 Ω Guildline standard resistance. Calibration time was controlled by a home-made timer-counter with an accuracy of ±0.01 s.

The temperature changes inside the reaction vessel were recorded to 10^{-4} K at fixed intervals of 10 s by a Hewlett-Packard quartz thermometer (HP 2804A) and printer (HP 5150A). The quartz thermometer probe fitted tightly into a glass tube filled with silicone oil to improve the thermal conductivity.

Sample ampoules were broken, one at a time, by a SiC needle (8) mounted on the upper propeller (16).

Results and discussion

Enthalpies of formation of sodium alkoxides can be calculated by using Scheme 1 and Eq. 3, where ΔH_r is the experimental enthalpy of reaction, ΔH_{d2} the enthalpy of solution of NaOH in water, and ΔH_{d3} the enthalpy of solution of the alcohol in H_2O + NaOH.

$$\Delta H_f^0(\mathrm{NaOR,cr}) = \Delta H_f^0(\mathrm{NaOH,cr}) + \Delta H_f^0(\mathrm{ROH,l/cr}) - \Delta H_f^0(\mathrm{H_2O,l}) - \Delta H_r + \Delta H_{d2} + \Delta H_{d3} \qquad (3)$$

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

Scheme 1

Table 1

Auxiliary thermochemical data

Compound	ΔH_f^0 (kJ/mol)	Ref.
H_2O,l	-285.83	9
CH_3OH,l	-239.1 ± 0.3	13
$CH_3OH \cdot \infty H_2O$	-246.4 ± 0.3	13
C_2H_5OH,l	-277.5 ± 0.4	13
$C_2H_5OH \cdot \infty H_2O$	-288.2 ± 0.4	13
i-C_3H_7OH,l	-318.1 ± 0.5	13
C_4H_9OH,l	-327.3 ± 0.4	13
t-C_4H_9OH,l	-359.2 ± 0.8	13
2-$C_5H_{11}OH$,l	-365.2 ± 1.1	13
C_6H_5OH,cr	-165.1 ± 0.8	13
NaOH,cr	-425.609	9
$NaOH \cdot \infty H_2O$	-470.11	9
NaCl,cr	-411.153	9
$HCl \cdot 552H_2O$	-166.596	9

Table 2

Enthalpies of solution of alcohols, ΔH_{d3} and ΔH_{d6}

Alcohol	ΔH_{d3} (kJ/mol) [a]	ΔH_{d6} (kJ/mol)
CH_3OH	-7.3 ± 0.4 [b]	-6.67 ± 0.74
C_2H_5OH	-10.7 ± 0.6 [b]	
i-C_3H_7OH	-13.18 ± 0.83	
C_4H_9OH	-7.75 ± 0.39	
	-7.39 ± 0.59 [c]	
t-C_4H_9OH	-14.67 ± 0.54	-7.2 ± 0.6
2-$C_5H_{11}OH$	-8.1 ± 1.0	
C_6H_5OH	-16.38 ± 0.43	12.4 ± 1.2

[a] In H_2O+NaOH solution, unless stated otherwise. [b] In H_2O. Calculated from data in ref. 9. [c] In H_2O.

Table 3

Reaction enthalpies and enthalpies of formation. Data in kJ/mol

R	ΔH_r [a]	ΔH_f^0(NaOR,cr) [a]
CH_3	-58.3 ± 2.4	-372.4 ± 2.4
	-113.6 ± 3.0 [b]	-375.7 ± 3.1 [b]
C_2H_5	-60.9 ± 1.8	-411.6 ± 1.9
i-C_3H_7	-54.0 ± 1.5	-461.6 ± 1.7
C_4H_9	-55.4 ± 5.0	-463.9 ± 5.0
t-C_4H_9	-82.2 ± 4.2	-475.9 ± 4.3
	-131.7 ± 4.0 [b]	-478.2 ± 4.1 [b]
2-C_5H_{11}	-71.7 ± 1.6	-485.9 ± 2.2
C_6H_5	-39.5 ± 3.6	-326.2 ± 3.7
	-64.5 ± 5.6 [b]	-331.6 ± 5.8 [b]

[a] Data for reaction 1, unless stated otherwise. [b] Data for reaction 2.

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

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

Scheme 2

The concentrations of NaOH in solution were always very low (about 1 mol of NaOH to 4.2×10^5 mol of water). As this is effectively close to infinite dilution, the value of the enthalpy of solution of NaOH in water (ΔH_{d2}) can be calculated as -44.5 kJ/mol, by using data in Table 1. Enthalpies of solution for the various alcohols, ΔH_{d3}, are presented in Table 2. Values for R = Me, 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 the values of 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 + NaOH (Table 2). The values for ΔH_r and the enthalpies of formation calculated from Scheme 1 are presented in Table 3.

As referred above, the thermochemical study of reaction 2 provides an alternative method of obtaining the enthalpies of formation of the alkoxides, Scheme 2 and Eq. 4. ΔH_r is the experimental enthalpy of reaction, ΔH_{d5} the enthalpy of solution of NaCl in HCl aqueous solution, ΔH_{d6} the enthalpy of solution of the alcohol in HCl aqueous solution + NaCl, and ΔH_{d7} the enthalpy of solution of water in 0.1 N HCl.

$$\begin{aligned}\Delta H_f^0(\mathrm{NaOR,cr}) = {} & \Delta H_f^0(\mathrm{NaCl,cr}) + \Delta H_f^0(\mathrm{ROH,l/cr}) - \Delta H_f^0(\mathrm{HCl \cdot 552H_2O}) \\ & - \Delta H_r + \Delta H_{d5} + \Delta H_{d6} + 552\ \Delta H_{d7} \end{aligned} \qquad (4)$$

ΔH_{d7} was found to be very close to zero (≈ 0.005 kJ/mol) and neglected. ΔH_{d5} was also measured and observed to be slightly concentration-dependent in the range 4×10^{-3}–22×10^{-3} M. In order to derive the ΔH_{d5} values corresponding to the stoichiometric amounts of NaCl produced (n), Eq. 5 was used.

$$\Delta H_{d5} = (0.995 \pm 0.070) + (718 \pm 35)\ n\ (\mathrm{kJ/mol}) \qquad (5)$$

Linear regression (correlation coeficient 0.9999) led to $\Delta H_{d5} = 1.08 \pm 0.07$, 1.10 $\pm$ 0.07, and 1.12 ± 0.08 kJ/mol for the experiments involving NaOMe, NaO-t-Bu, and NaOPh, respectively. The enthalpies of solution ΔH_{d6} are shown in Table 2. The enthalpies of reaction and the derived enthalpies of formation are presented in Table 3.

There is a good agreement between the enthalpies of formation of sodium alkoxides derived from Schemes 1 and 2, Table 3, supporting the reliability of these data. The only available literature value, $\Delta H_f^0(\mathrm{NaOEt,cr}) = -410.0 \pm 4.2$ kJ/mol [4], agrees within experimental uncertainties with that obtained in the present study.

The data in Table 3 can be subject to a consistency test involving a plot of the enthalpies of formation of the crystalline n-alkyl 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 atmosphere). This type of plot has been used before to assess the reliability of thermochemical data for many families of com-

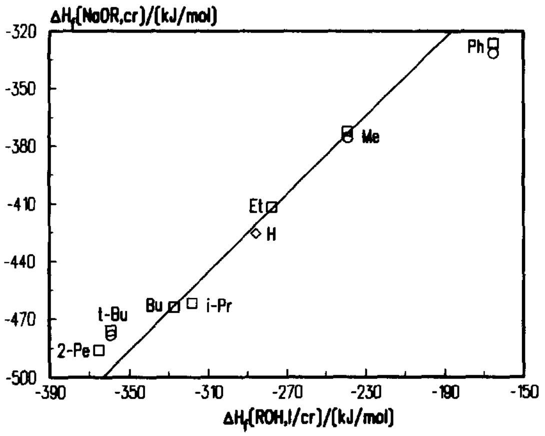

Fig. 2. Enthalpies of formation of sodium alkoxides versus enthalpies of formation of the corresponding alcohols. Data from reaction 1 (squares), from reaction 2 (circles), and ref. 9 (diamond).

pounds [5,6]. In the present case a good linear correlation ($r = 0.9993$; uncertainty intervals are standard deviations), Eq. 6, is observed as shown in Fig. 2.

$$\Delta H_f^0(\mathrm{NaOR,cr}) = (1.017 \pm 0.026)\ \Delta H_f^0(\mathrm{ROH,cr/l}) - (130.6 \pm 7.2) \qquad (6)$$

This correlation also fits the points for R = H and i-Pr but those for R = t-Bu and 2-Pe clearly fall above the line. Steric effects may be responsible for the destabilization of NaO-t-Bu and NaO-2-Pe; the destabilization can be quantified as ca. 19 and 16 kJ/mol, respectively. It must be stressed that these destabilization enthalpies are relative to the corresponding alcohols, i.e. the above values measure the effect of replacing an hydrogen by a sodium atom. An alternative and perhaps more likely explanation for the "high" values of ΔH_f^0(NaO-t-Bu,cr) and ΔH_f^0(NaO-2-Pe,cr) may be related with the solid state structures of these alkoxides, which unfortunately are not available. Ionic-type structures may be more favoured for smaller alkyl groups than for longer or bulky alkyl chains. This is also suggested by the deviation observed for the octyl (Oc) analogue, the results for which are not shown in Table 3. Experiments involving NaOOc, using a 1 : 1 water-tetrahydrofuran mixture as reaction medium, led to $\Delta H_f^0(\mathrm{NaOOc,cr}) = -526.3 \pm 4.8$ kJ/mol, which is about 40 kJ/mol higher than predicted by Eq. 6 [7*]. If this result is correct, then the correlation must be used with caution for estimating the standard enthalpies of formation of alkoxides with long alkyl chains.

$$\begin{tikzcd}
\mathrm{NaOR(cr)} \arrow[d, "\Delta H^0_{\mathrm{sub1}}"] & + & \mathrm{H_2O(l)} \arrow[d, "\Delta H^0_{\mathrm{vap1}}"] \arrow[r, "\Delta H^0_r"] & \mathrm{ROH(cr/l)} \arrow[d, "\Delta H^0_{\mathrm{vap2}}"] & + & \mathrm{NaOH(cr)} \arrow[d, "\Delta H^0_{\mathrm{sub2}}"] \\
\mathrm{NaOR(g)} & + & \mathrm{H_2O(g)} \arrow[r, "\Delta H^0_g"] & \mathrm{ROH(g)} & + & \mathrm{NaOH(g)}
\end{tikzcd}$$

Scheme 3

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[*] Reference number with asterisk indicates a note in the list of references.

An interpretation of Fig. 2 can be based on Scheme 3 or Eqs. 7 and 8.

$$\Delta H_f^0(\mathrm{NaOR,cr}) = \Delta H_f^0(\mathrm{ROH,cr/l}) + \Delta H_f^0(\mathrm{NaOH,cr}) - \Delta H_f^0(\mathrm{H_2O,l}) - \Delta H_r^0 \quad (7)$$

$$\begin{aligned}\Delta H_r^0 &= \Delta H_g^0 + \left(\Delta H_{\mathrm{sub1}}^0 - \Delta H_{\mathrm{sub2}}^0\right) - \left(\Delta H_{\mathrm{vap2}}^0 - \Delta H_{\mathrm{vap1}}^0\right)\\ &= \mathrm{D(Na{-}OR)} - \mathrm{D(H{-}OR)} + \mathrm{D(H{-}OH)} - \mathrm{D(Na{-}OH)}\\ &\quad + \Delta\left(\Delta H_{\mathrm{sub}}^0\right) + \Delta\left(\Delta H_{\mathrm{vap}}^0\right) \qquad (8)\end{aligned}$$

Equations 6 and 7 indicate that ΔH_r^0 is constant for the alkoxides which fit the linear correlation. Moreover, Eq. 7 predicts that the slope should be unity, in keeping with Eq. 6. A better understanding of these observations can be obtained in terms of Eq. 8. Here, $\Delta H_{\mathrm{sub}}^0$ and $\Delta H_{\mathrm{vap}}^0$ 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(Na–OR), D(H–OH), D(H–OR), and D(Na–OH) are bond dissociation enthalpies. The constancy of ΔH_r^0 and the reasonable assumption that the differences between the sublimation and the vaporization enthalpies cancel each other [5,6] suggests that the difference D(Na–OR) – D(H–OR) is also constant. This conclusion can be used to estimate a rough value of D(Na–OR), since H–OR bond dissociation enthalpies fall in a narrow range [8]. A mean value, ⟨D(H–OR)⟩ = 435 ± 3 kJ/mol, together with D(H–OH) = 499 kJ/mol, D(Na–OH) = 353 kJ/mol [9], and auxiliary data from Table 1, leads to ⟨D(Na–OR)⟩ ≅ 280 kJ/mol. It should be remembered that this value is applicable for the alkoxides that fit the correlation in Fig. 2.

As remarked for the sodium alkoxides, there are almost no thermochemical values for other alkali metal alkoxides. It is possible to use the above linear correlation and the few available literature data speculatively to assess or to estimate new standard enthalpies of formation for those alkaline metal alkoxides. Figure 3 shows a plot of $\Delta H_f^0(\mathrm{MOR,cr})$ vs. $\Delta H_f^0(\mathrm{ROH,l/cr})$ for M = Li, K, Rb, and Cs and R = H and Et [4,9,10]. The straight line drawn in this figure, which is the same as that in Fig. 2 (i.e. Eq. 6), fits all the data except those for lithium. The

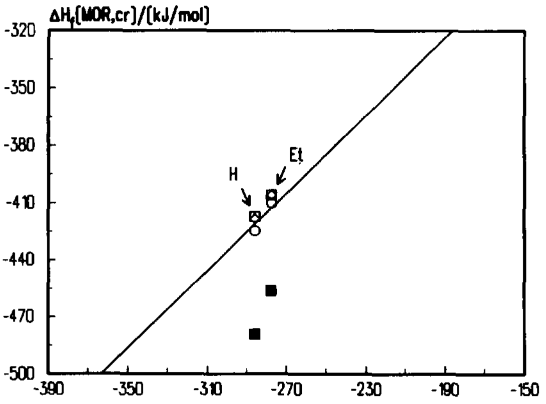
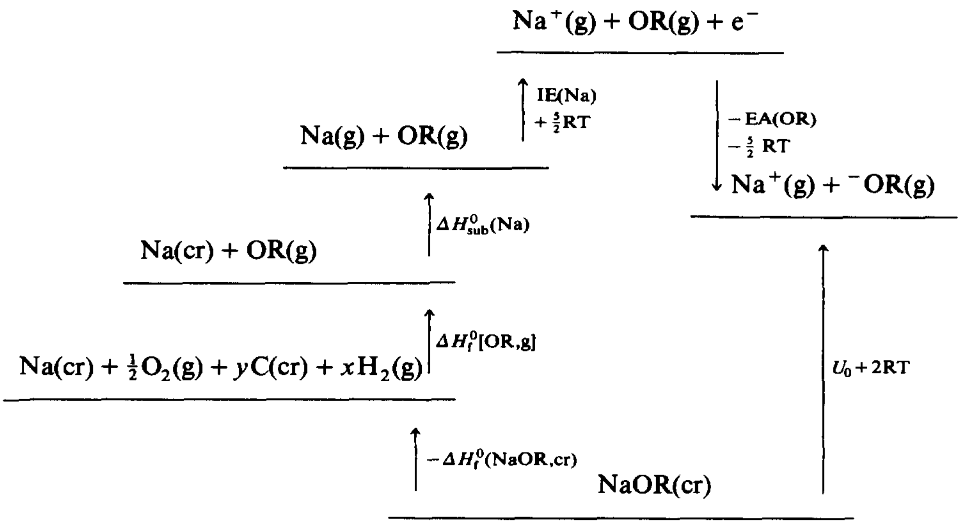


Fig. 3. Enthalpies of formation of alkaline metal alkoxides versus enthalpies of formation of the corresponding alcohols. M = Li (full squares), K (circles), Rb (diamonds), and Cs (squares). The line is the same as in Fig. 2.



Scheme 4

surprising feature of Fig. 3 is perhaps the fact that the data for Na, K, Rb, and Cs fall in the same line, instead of defining a series of lines with similar slopes but different intercepts [5,6].

The lattice energy, U_0, of the sodium alkoxides can be calculated from Scheme 4 by using the derived enthalpies of formation. The values (Table 4) are rather high, only 50 kJ/mol lower than the lattice energy of sodium hydroxide, indicating a strong ionic nature of Na-OR bonds. This can perhaps be better appreciated when the lattice energy is broken down into two terms, the enthalpy of sublimation of the sodium alkoxide, $\Delta H^0_{\mathrm{sub}}$(NaOR), and the Na–OR heterolytic bond dissociation enthalpy, D_{het}(Na–OR), Scheme 5.

Estimates of D_{het}(Na–OR) for R = n-alkyl were made by using the above value for ⟨D(Na–OR)⟩, 280 kJ/mol, together with the ionization energy of Na and the electron affinity of RO. The results (Table 4) were then used to derive the sublimation enthalpies, also collected in Table 4. It is noteworthy that $\Delta H^0_{\mathrm{sub}}$(NaOR)

Table 4

Lattice energies of sodium alkoxides. Estimates of enthalpies of sublimation and heterolytic Na^+–OR^- bond dissociation enthalpies. Data in kJ/mol.

R	ΔH_f^0(RO,g) [a]	EA(OR) [b]	U_0 [c]	$\Delta H^0_{\mathrm{sub}}$	D_{het}
H	39 ± 4	176.4 ± 1.0	886.4 ± 4.1	218.5	672.9
CH_3	18 ± 4	151.4 ± 2.1	837.0 ± 5.1	218	624
C_2H_5	−17 ± 4	166.5 ± 3.2	826.2 ± 5.5	222	609
i-C_3H_7	−52 ± 4	177.4 ± 2.8	830.3 ± 5.2	237	598
C_4H_9	−63 ± 4	171 ± 14	827 ± 15	227	605
t-C_4H_9	−91 ± 5	184.4 ± 5.2	798.5 ± 8.4		
2-C_5H_{11}	−105 ± 8 [d]	186.2 ± 4.8	792.8 ± 9.6		
C_6H_5	48 ± 8	213 ± 18	747 ± 20		

[a] Data from ref. 8. [b] Data from ref. 14. [c] IE(Na) = 495.84 kJ/mol and $\Delta H^0_{\mathrm{sub}}$(Na) = 107.32 kJ/mol (ref. 9). [d] Estimated value.

$$\begin{tikzcd}
\mathrm{NaOR(cr)} \arrow[r, "\Delta H^0_{\mathrm{sub}}"] \arrow[rr, bend left, "U_0 + 2\mathrm{RT}"] & \mathrm{NaOR(g)} \arrow[r, "\mathrm{D_{het}(Na{-}OR)}"] \arrow[dr, "\mathrm{D(Na{-}OR)}"'] & \mathrm{Na^+(g) + RO^-(g)} \\
& & \mathrm{Na(g) + RO(g)} \arrow[u, shift right=3, "\mathrm{EI(Na)}"'] \arrow[u, shift left=3, "-\mathrm{EA(RO)}"]
\end{tikzcd}$$

Scheme 5

Table 5

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

R	r_{therm}
H	140
CH_3	154
C_2H_5	157
i-C_3H_7	156
C_4H_9	157
t-C_4H_9	166
2-C_5H_{11}	168
C_6H_5	185

[a] $r_+(Na^+) = 102$ pm.

increases slightly with the size of the alkyl chain but the opposite trend observed for $D_{het}(Na{-}OR)$ dominates the sum. These considerably high values can be compared, for instance, with $D_{het}(Na{-}Cl) = 552.9$ kJ/mol.

Accepting the ionic nature of sodium alkoxides, thermochemical radii of the anions RO^- were calculated by using the Kapustinskii approximation, Eq. 9 [11,12]. Here, ν is the number of ions in one molecule, z_+ and z_- are the charges of Na^+ and RO^-, and r_+ and r_- are the respective thermochemical radii in pm. The results for r_- are presented in Table 5.

$$U_0 = \frac{1.079 \times 10^5\ \nu\, z_+ z_-}{r_+ + r_-} \tag{9}$$

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7 The water + THF mixture was required due to solubility problems of octanol in water. The details of thermochemical results are as follows (kJ/mol): $\Delta H_r = -59.1 \pm 1.2$, $\Delta H_{d1} = 0.82$, $\Delta H_{d2} = -29.7 \pm 4.2$, $\Delta H_{d3} = 11.4 \pm 2.1$. These quantities have the meaning indicated for Scheme 1. The enthalpy of formation of liquid octanol was taken as -426.5 ± 0.7 kJ/mol (ref. 12).

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