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"Inverted" Sodium–Lithium Electronegativity: Polarity and Metalation Energies of Organic and Inorganic Alkali-Metal Compounds

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The polarity and the metalation energies of selected organic and inorganic alkali-metal compounds MR (R = H, CH_3, NH_2, OH, F, η^5-C_5H_5), studied by ab initio pseudopotential calculations, show *two types* of behavior, both *monotonous* and *nonmonotonous*, along the Li–Cs series. The MX bonds in the NH_2, OH, F, and η^5-C_5H_5 derivatives are almost completely ionic, and the Li to Cs trends are *monotonous*. In contrast, alkali-metal hydrides and methides show some covalent character and a *nonmonotonous* behavior of the metal charges ρ along the series $\rho_{Li} > \rho_{Na} < \rho_K < \rho_{Rb} < \rho_{Cs}$. This trend, which parallels the Allred–Rochow electronegativities of the alkali metals, is attributed to varying covalent σ contributions to the MX bonding. The covalent bonding contributions in MH and MCH_3 influence the energies of metalation of the NH_3, H_2O, HF, and C_5H_6 set and results in nonmonotonous behavior down group I. In contrast, the metalation energies within one of these sets, e.g. the reaction energies of H_2 with MCH_3 or the reaction energies involving only NH_2, OH, F, or C_5H_5 derivatives, are almost independent of the metal.

Introduction

According to textbook wisdom "the ionic character of the M–C bond increases from Li to Cs".[1] The real situation is far more complex. More than 30 years ago, Allred and Rochow deduced that the electronegativity of Na is *greater* than that of Li.[2] Other electronegativity scales (Figure 1) show varying but nonlinear behavior from Li to Cs.[3] Indeed, the electronegativity of the second member of many other groups appears to be anomalous.[3d] The changes in the ionization potential of the alkali metals are also not regular[4] (Figure 2).

We investigate in this paper the variations in the ionicity and the reaction energies in different alkali-metal compounds (MX; X = H, CH_3, NH_2, OH, F, η^5-C_5H_5 (Cp)). We find two types of behavior.

Despite the importance of alkali-metal organic compounds in synthetic organic chemistry,[5] little is known about the group I (Li–Cs) energetic trends: e.g., the homo- and heterolytic X–M (M = Li–Cs) dissociation energies, solvation energies, heats of protolysis reactions, etc. Attempts to measure thermodynamic properties in solution suffer from a lack of information about the exact systems involved.[6] Many alkali-metal compounds form equilibria of different aggregates in solution and/or of contact and solvent-separated ion pairs.[7] While high-level ab initio all-electron calculations of the heavier alkali-

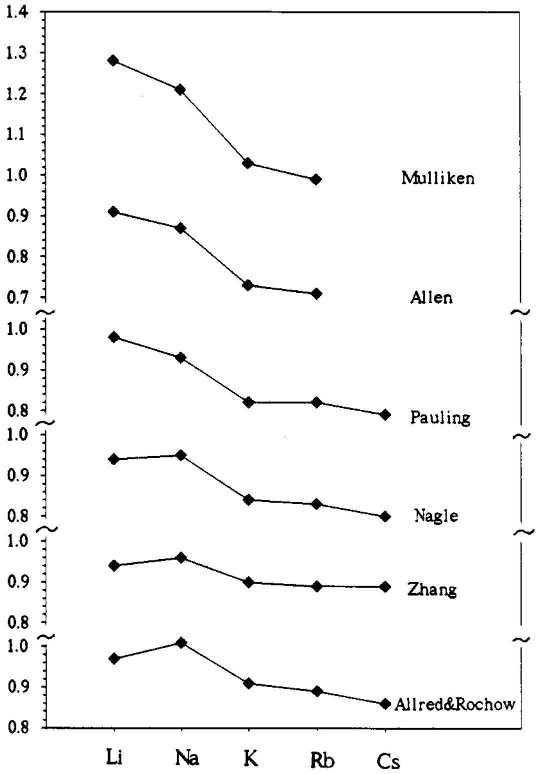

Figure 1. Electronegativities of the alkali metals.[2,3]

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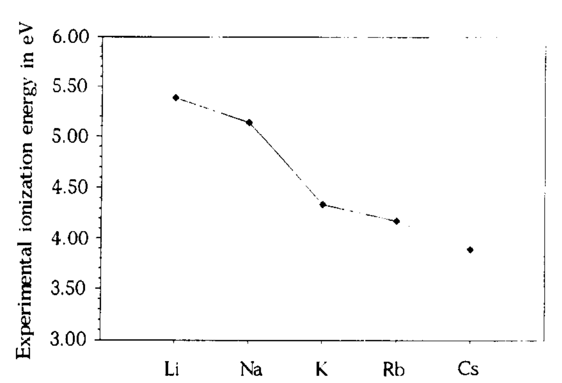

Figure 2. Experimental ionization energies of the alkali metals.[4]

metal compounds can yield data on well-defined species, they have been restricted to very small systems. The questions we wish to answer are as follows. Why do MH and MCH_3 show a nonmonotonous behavior of polarity on going from Li to Cs, while derivatives MX of π-donating substituents (X = OH, NH_2, F, Cp) do not? What is the effect of the polarity on the relative metalation energies of NH_3, H_2O, HF, and CpH with MH or MCH_3?

We use the pseudopotential method[8] to study representative alkali-metal model compounds, e.g. to evaluate the polarity and the relative metalation energies. Alkali-metal hydrides and methides serve as models for slightly covalent alkali-metal alkyl derivatives, hydroxides for alkoxides, amides for dialkylamides, and cyclopentadienides for typical π-bound organometallic species.

Computational Methods

Compared to all-electron calculations,[9] the use of pseudopotentials to replace the core electrons considerably diminishes the computational costs for compounds of the heavier elements K, Rb, and Cs. For consistency, we employed quasirelativistic one-valence-electron pseudopotentials (1-ve-ecp) from Fuentealba et al.[9b] to calculate the Li and Na compounds. In contrast to the case for the ligher alkali metals, the core polarizability is significant for the heavier alkali metals K–Cs.[10] Thus, we used nine-valence-electron (valence plus $n-1$ shell) pseudopotentials for K, Rb, and Cs,[11] as the implicit frozen-core approximation leads to large errors in a 1-ve-ecp treatment. For C, N, O, and F, the pseudopotentials of Igel-Mann et al. and Dolg[12] replace the [1s] cores.

Triple-ζ valence basis sets augmented with p and d polarization functions (211/31/1) were employed for Li and Na.[13,14] More flexible (21111/21111/11) valence basis sets[11] including two uncontracted d functions from Huzinaga et al.[14] were used for the heavier alkali metals (K, Rb, Cs). For the geometry optimization of the metal cyclopentadienides we employed a double-ζ valence basis set with one d polarization function (DZP) (31/31/1) on carbon[13] and a double-ζ (DZ) (31) hydrogen basis set from Dunning and Hay.[15] For all other optimizations and all single-point calculations, C, N, O, and F basis sets of double-ζ quality[13,16] were augmented with d polarization functions[14] and a single diffused sp set[17] (311/311/1). The hydrogen basis set was of triple-ζ quality with two uncontracted sets of p functions (311/11).[18]

All geometries were optimized at Hartree–Fock level (HF), using the gradient optimization techniques implemented in the GAUSSIAN 88[19] and GAUSSIAN 90[20] program packages. For K–Cs, the metal–substituent distances *d*(M–S) of all species with the exception of MCp were optimized at the MP2(FU) level with fixed HF geometry for the substituent (by fitting a set of single-point calculations to a third-order polynomial). The optimization procedure for MCp was somewhat different from that for the other compounds. All alkali-metal cyclopentadienides were first optimized at the HF level with the smaller (3111/3111/2) basis sets for K, Rb, and Cs, the (31/31/1) DZP carbon basis, and the DZ basis for hydrogen. The fixed-ring geometry was used to optimize the M–ring distances at the HF and MP2 levels with the extended metal basis sets (21111/21111/2) for K, Rb, and Cs. We assume the smaller basis set without diffuse functions on carbon to be sufficient for geometry optimizations, since the negative charge on the substituent is delocalized. However, for the evaluation of the total energies (MP2) and for the population analyses, we carried out single-point calculations using the extended basis sets for the metals, carbon, and hydrogen. Substituent (CH_3, NH_2, OH, and Cp) geometries were not optimized at the MP2 level since the influence of electron correlation on the geometries is expected to be small, as was shown with M = Li, Na (cf. Appendix, Table V). The very small effects of valence correlation on the MX distances with M = Li, Na also have been neglected (cf. the MP2 all-electron calculations for Li and Na species in Table V).

Electron correlation effects on the relative energies were corrected by single-point calculations with second- and fourth-order Møller–Plesset perturbation theory (MP2(FU) and MP4SDTQ(FU)) at the HF-optimized geometries for Li and Na and at the MP2-optimized geometries for K–Cs. Natural population analyses (NPA)[21] of the SCF densities also have used these geometries. Relative energies were not corrected for zero-point energies, as these contributions are quite small.

Results and Discussion

A. Population Analysis of the Wave Function. The Allred–Rochow electronegativity scale[2] indicates that Na is more electronegative than Li, while the electronegativity slightly decreases from Na to Cs. Only a few other scales also show a nonmonotonous trend along the series Li–Cs (see Figure 1). However, in most of the electronegativity scales that exhibit a *monotonous* increase within group I from Cs to Li, the curve flattens somewhat on going from

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Table I. Natural Charges on the Metal at the HF Level[a]

	Li	Na	K	Rb	Cs
MH	0.83	0.78	0.86	0.86	0.88
MCH_3	0.87	0.79	0.90	0.90	0.93
MNH_2	0.95	0.97	0.99	0.99	0.98
MOH	0.97	0.99	1.00	1.00	0.99
MF	0.98	0.99	0.99	0.99	0.98
MCp	0.91	0.95	0.98	0.98	0.96

[a] The gap after the first two rows shows the separation between "slightly covalent" (above) and fully ionic (below) species. One-valence-electron effective core potentials (1-ve-ecp's) are given for Li and Na, 9-ve-ecp's are given for K–Cs and 4-, 5-, 6-, 7-ve-ecp's are given for C, N, O, and F. Basis set contraction scheme: Li, Na (211/31/1); K–Cs (21111/21111/11); C, N, O, F (311/311/1); H (311/11). HF-optimized geometries (Li, Na) and MP2-optimized geometries (K–Cs) were used and are specified in Table V.

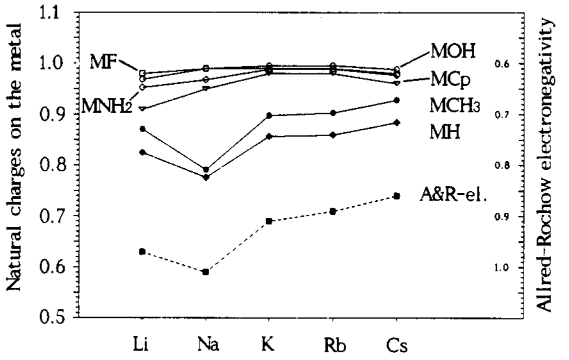

Figure 3. Natural charges (NPA) on the metal at the HF level (left scale) for the MX compounds (X = CH_3, H, NH_2, OH, F, Cp) and Allred–Rochow electronegativities (right scale) of the alkali metals. For the specification of the basis set see footnote *a* in Table I.

Na to Li (e.g. Mulliken,[3d] Allen,[3d] Pauling[2]). The metal electronegativity should be an indicator for the polarity of the MX (M = Li–Cs) bonds. Schade and Schleyer[22] found earlier that the metal charge in $NaCH_3$ is less than in $LiCH_3$. Similar behavior was noted for LiH and NaH by Bader.[23]

The NPA metal charges for the alkali-metal hydrides, methides, amides, hydroxides, fluorides, and cyclopentadienides and the Allred–Rochow electronegativities[2] for the alkali metals (cf. Table I) are plotted in Figure 3. We find two different polarity trends: while the charges ρ in MNH_2, MOH, MF, and MCp increase smoothly from Li to Rb, the charges for the hydrides and methides exhibit a nonmonotonous trend: $\rho_{Li} > \rho_{Na} < \rho_{K} < \rho_{Rb} < \rho_{Cs}$. The metal charges are in general significantly higher for MNH_2, MOH, MF, and MCp than for MH and MCH_3. Hence, we define two groups of alkali-metal compounds: the almost completely ionic derivatives of highly electronegative substituents MX (X = NH_2, OH, F, Cp) with π-donating[24] character and more covalent derivatives with less electronegative and almost exclusively σ-donating substituents (MH, MCH_3).

A more detailed analysis of the natural populations (see Table II) shows that the s-orbital occupation on the metal is only significant throughout the second set of compounds (MH, MCH_3) and, to a lesser extent, for the Li and Na species of the ionic set of compounds. The s populations for MH and MCH_3 correlate with the Allred–Rochow electronegativities (note that this also holds true for the much smaller s populations in MNH_2). d_{z^2} populations are appreciable for all Cs species (with the exception of CsCp) but exceed the s populations only for $CsNH_2$, CsOH, and CsF. Significant π populations are found for $LiNH_2$, $CsNH_2$ and LiCP, NaCp, and CsCp. While the net populations of the MH and MCH_3 derivatives are mainly due to the σ contributions (mainly s, but for Cs also some d_{z^2} contributions), the net populations are a sum of s, p, and d populations ($\sigma + \pi$ contributions) in MNH_2, MOH, MF, and MCp. Cp^- is known to be a strong π donor. This is apparent in the alkali-metal cyclopentadienides: the metals exhibit higher π than σ populations.[25] Note that in the highly ionic alkali-metal derivatives Cp^- acts as a σ *and* a π donor, whereas in the more covalent transition-metal compounds it is a σ donor and a π acceptor.[26]

We find it useful to distinguish between σ and π electronegativity following the concept of orbital electronegativity by Hinze, Whitehead, and Jaffé.[27] These authors conceive electronegativity as a property of an atom not in its ground state but in its valence state. The alkali-metal compounds studied here can roughly be separated into slightly covalent σ-bound derivatives (MH, MCH_3) and into the more ionic compounds where σ and π orbitals are involved (MNH_2, MOH, MF, MCp). The σ electronegativities dominate in MH and MCH_3. In these compounds Li is less electronegative than Na. The polarities parallel the alkali-metal electronegativities of the Allred–Rochow scale, which can be conceived in these cases as a σ-electronegativity scale. In species with the more electronegative, potentially π-donating substituents (NH_2, OH, F, Cp), however, π electronegativities also have to be considered. The sums of the σ and the π populations, and thus the electronegativities, appear to be almost equal for all the alkali metals. As a result, a small decrease of the metal net populations from Li to Rb and a small increase from Rb to Cs are observed for these derivatives.

B. Reaction Energies. Since covalent contributions strengthen the bonds, the different degrees of ionicity influence the relative metalation energies of alkali-metal compounds. The metalation energies of NH_3, H_2O, HF, and CpH with MCH_3 (eqs 2–5) are all exothermic but exhibit a nonmonotonous trend (see Figure 4 and Table III) along the series Li–Cs. While these reaction energies *decrease* from Cs to Na, they *increase* from Na to Li. The reaction energies of MH with NH_3, H_2O, HF, and CpH (e.g. eqs 6 and 7; see Table IV) show a similar behavior. In contrast, the reaction energy of MCH_3 with H_2 is almost independent of the metal (eq 1). The metal independence also is found for metalation reactions involving only MNH_2,

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Table II. SCF Natural Populations on the Metal for MX (X = CH_3, H, NH_2, OH, F, Cp)[a]

	MCH_3					MH				
	Li	Na	K	Rb	Cs	Li	Na	K	Rb	Cs
s	0.118	0.208	0.100	0.097	0.054	0.162	0.220	0.135	0.133	0.095
p_x										
p_y										
p_z	0.010	0.002	0.001	0.001		0.013	0.004	0.006	0.007	0.005
d_{xy}										
d_{xz}			0.001	0.001	0.001			0.001	0.001	0.001
d_{yz}			0.001	0.001	0.001			0.001	0.001	0.001
$d_{x^2-y^2}$										
d_{z^2}	0.001		0.006	0.008	0.032			0.007	0.008	0.029
$s + p_z + d_{z^2}$[b]	0.129	0.210	0.107	0.106	0.086	0.175	0.224	0.148	0.148	0.129

	MNH_2					MOH				
	Li	Na	K	Rb	Cs	Li	Na	K	Rb	Cs
s	0.023	0.027	0.008	0.008	0.006	0.016	0.009	0.002	0.003	0.004
p_x	0.020	0.004	0.001			0.006				
p_y	0.001	0.001	0.001			0.006				
p_z	0.004		0.001	0.001	0.001	0.002		0.001	0.001	0.001
d_{xy}										
d_{xz}			0.003	0.004	0.001			0.003	0.004	0.008
d_{yz}			0.001	0.001	0.012			0.003	0.004	0.008
$d_{x^2-y^2}$										
d_{z^2}			0.007	0.007	0.021			0.005	0.006	0.014
$s + p_z + d_{z^2}$[b]	0.029	0.027	0.016	0.016	0.028	0.018	0.009	0.008	0.010	0.019

	MF					MCp				
	Li	Na	K	Rb	Cs	Li	Na	K	Rb	Cs
s	0.007	0.007	0.002	0.003	0.003	0.033	0.020	0.010	0.009	0.007
p_x	0.005					0.027	0.013	0.003	0.001	
p_y	0.005					0.027	0.013	0.003	0.001	
p_z	0.006		0.001	0.001	0.001	0.002	0.001			
d_{xy}										
d_{xz}	0.001		0.003	0.003	0.006			0.005	0.006	0.016
d_{yz}	0.001		0.003	0.003	0.006			0.005	0.006	0.016
$d_{x^2-y^2}$										
d_{z^2}			0.010	0.011	0.026	0.001		0.001	0.002	0.003
$s + p_z + d_{z^2}$[b]	0.013	0.007	0.013	0.015	0.030	0.036	0.021	0.011	0.011	0.010

[a] See footnote *a* in Table I. [b] Net σ population.

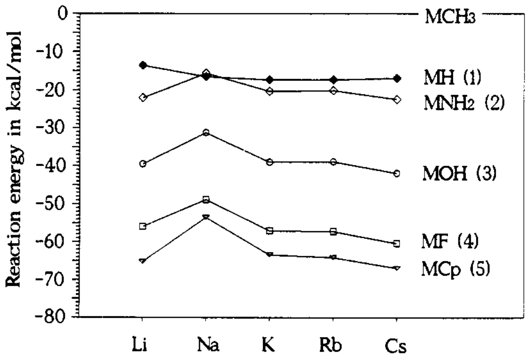

Figure 4. Reaction energies at the MP4 level for eqs 1–5 (MP2 for eq 5). For the specification of the basis set see footnote *a* in Table I.

MOH, MF, or MCp and NH_3, H_2O, HF, or CpH (see, e.g., eq 8; Table IV). The other reaction energies of this type can easily be evaluated by subtracting the appropriate reaction energies of eqs 2–5.

For comparison, reaction energies for eqs 6–8 also were calculated from experimental homolytic dissociation energies (D_e) and are displayed together with the theoretical values in Figure 5. The agreement is reasonable in view of the large uncertainty (ca. >±4 kcal/mol) of the experimental data (Table IV).

The correlation between the polarity of the slightly covalent set of compounds (MH or MCH_3) and the reaction energies between MCH_3 or MH and NH_3, H_2O, HF, or CpH (e.g. eq 2: $MCH_3 + NH_3 \rightarrow CH_4 + MNH_2$) can be explained in terms of the increasing covalency and thus the increasing stability of, for example, MCH_3 vs MNH_2 from Cs to Na. Extrapolation of the metalation energy

Table III. Reaction Energies in kcal/mol for Eqs 1–5[a]

	(1) $MCH_3 + H_2 \rightarrow MH + CH_4$			(2) $MCH_3 + NH_3 \rightarrow MNH_2 + CH_4$		
	HF	MP2(FU)	MP4(FU)	HF	MP2(FU)	MP4(FU)
Li	−19.2	−11.8	−13.6	−23.1	−22.5	−22.0
Na	−23.1	−14.3	−16.5	−17.0	−16.1	−15.6
K	−24.6	−15.3	−17.3	−22.0	−20.7	−20.3
Rb	−24.9	−15.2	−17.3	−21.9	−20.6	−20.1
Cs	−24.4	−14.9	−16.9	−23.4	−22.9	−22.4

	(3) $MCH_3 + H_2O \rightarrow MOH + CH_4$			(4) $MCH_3 + HF \rightarrow MF + CH_4$		
	HF	MP2(FU)	MP4(FU)	HF	MP2(FU)	MP4(FU)
Li	−42.5	−39.9	−39.4	−59.9	−55.8	−55.9
Na	−35.2	−31.7	−31.2	−54.6	−48.7	−48.8
K	−43.0	−39.3	−38.9	−63.7	−56.7	−57.1
Rb	−43.0	−39.2	−38.8	−64.2	−57.0	−57.3
Cs	−44.8	−42.1	−41.9	−66.0	−59.7	−60.4

	(5) $MCH_3 + CpH \rightarrow MCp + CH_4$ MP2(FU)		(5) $MCH_3 + CpH \rightarrow MCp + CH_4$ MP2(FU)
Li	−65.2	Rb	−64.1
Na	−53.5	Cs	−66.9
K	−63.4		

[a] See footnote *a* in Table I.

Table IV. Calculated (MP4(FU)) and Experimental Reaction Energies for Eqs 6–8 in kcal/mol[a]

	(6) $MH + H_2O \rightarrow MOH + H_2$		(7) $MH + HF \rightarrow MF + H_2$	
	MP4(FU)	exptl[b]	MP4(FU)	exptl[b]
Li	–25.8	–33.0 ± 2.1	–42.3	–48.0
Na	–14.7	–20.1 ± 3.2	–32.3	–36.2
K	–21.6	–27.7 ± 3.2	–39.8	–42.7
Rb	–21.6	–30.4 ± 3.9	–40.0	–42.2
Cs	–25.0	–32.8 [illegible] 2.1	–43.5	–45.0

	(8) $MOH + HF \rightarrow MF + H_2O$	
	MP4(FU)	exptl[b]
Li	–16.5	–15.9
Na	–17.6	–16.1
K	–18.2	–15.5
Rb	–18.5	–12.7
Cs	–18.5	–14.3

[a] See footnote *a* in Table I. [b] Experimental heats of reaction were calculated from D_e values or from D_0 values and zero-point vibrational corrections: D_e(LiH), ref 28; D_e(NaH, KH, RbH), ref 29; D_e(CsH), ref 30; D_e(MOH), ref 9e and literature cited therein; $D_e(H_2O, CH_4)$, ref 31; D_0, ω_e, $\omega_e x_e$ (MF, HF, H_2), ref 32. We estimate the error of the experimental reaction energies to be >±4 kcal/mol.

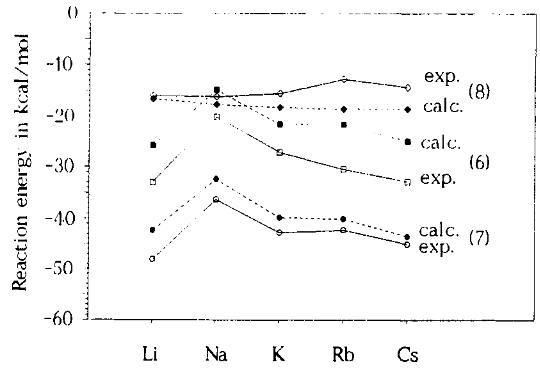

Figure 5. Comparison of the experimental and theoretical (MP4) reaction energies for eqs 6–8. For the specification of the basis set see footnote *a* in Table I.

$$MCH_3 + H_2 \rightarrow MH + CH_4 \quad (1)$$

$$MCH_3 + NH_3 \rightarrow MNH_2 + CH_4 \quad (2)$$

$$MCH_3 + H_2O \rightarrow MOH + CH_4 \quad (3)$$

$$MCH_3 + HF \rightarrow MF + CH_4 \quad (4)$$

$$MCH_3 + CpH \rightarrow MCp + CH_4 \quad (5)$$

$$MH + H_2O \rightarrow MOH + H_2 \quad (6)$$

$$MH + HF \rightarrow MF + H_2 \quad (7)$$

$$MOH + HF \rightarrow MF + H_2O \quad (8)$$

curve to Li would suggest an even smaller reaction energy. Instead, the reaction energy is larger due to the smaller covalent bonding contributions in $LiCH_3$. The same trend is observed for the reactions of MCH_3 (or MH) with all HX (X = NH_2, OH, F, Cp) compounds to give the MX derivatives. Reaction energies *within* the more ionic MX set or *within* the MH, MCH_3 set are essentially independent of the metal. For the first group of species (MX compounds), this is due to the overall high ionicity of the compounds. For the second group (MH, MCH_3), the reaction energies are independent of the metal because the covalent bonding contributions and thus the stabilities run parallel in the hydrides and in the methides. The reaction energies for a given metal are governed by the relative stabilities (basicities) of the free anions (H^-, CH_3^-, NH_2^-, OH^-, F^-, and Cp^-). Only for H^- vs NH_2^- is the order reversed compared to MH vs MNH_2.[32]

The Allred–Rochow electronegativities[2] estimate the relative polarity of the slightly covalent MH and MCH_3 compounds well, as can be seen from Figure 3. The Allred-Rochow scale is based on the Slater rules,[33] which estimate the shielding of nuclear charge by inner shells. The Slater rules, combined with the covalent radii, express the effective potential which binds a valence electron, i.e. its ionization potential (IP).[3b] The electronegativity scale of Zhang,[3b] which was derived directly from experimental ionization potentials, shows a trend similar to that for the Allred–Rochow scale. According to the Slater rules,[33] an electron of the $n - 1$ shell contributes *less* (0.85 au per electron for the $n - 1$ shell, cf. 1.00 au for the $n - 2$ etc. shells) than a unit charge to the shielding of the nuclear charge. Since the $n - 1$ shell of Li consists only of *two* electrons (in contrast to the $n - 1$ shell of the heavier alkali metals, which consists of *eight* electrons), the nuclear charge is *better* shielded (Z_{eff} is less) for Li than for Na–Cs. We stress that it is Li and not Na which steps out of a monotonous line of the electronegativity. The better shielding of the nuclear charge in Li can also be seen in the ionization potentials: the first ionization potential increases from Cs to Li due to the decreasing valence-electron to nucleus distances (covalent radii). However, the IP for Li is smaller than expected by extrapolation from K to Na[4] (see Figure 2) due to the better shielding provided by the $n - 1$ shell. Hence, an inherent atomic property—the relatively efficient shielding of the nuclear charge by the 1s electrons in Li (apparent in the first IP and the electronegativity scales by Allred–Rochow and by Zhang)—gives reason for the nonmonotonous behavior of ionicity in the slightly covalent compounds MH or MCH_3 (M = Li–Cs). In contrast, the MX (X = NH_2, OH, F, Cp) compounds are almost fully ionic. Moreover, whatever covalency there is shows a monotonous decrease from Li to Rb.

Conclusions

Li is less electronegative than Na in molecules with significant covalent σ-bonding contributions such as MH and MCH_3 (σ electronegativity). This is reflected in the Allred–Rochow electronegativity scale. In contrast, the MX derivatives with more electronegative substituents (X = NH_2, OH, F, Cp) are highly ionic. However, the small covalent contributions have both σ and π character. In these derivatives Li is more electronegative than Na (σ + π electronegativity) and a smooth increase in polarity is observed from Li to Rb. The different electronic structures of the ionic π-donor compounds MX and the somewhat covalent σ-donor systems (MH, MCH_3) influence the metalation energies directly. Due to the different

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degree of covalency, reactions involving MH or MCH_3 and NH_3, H_2O, HF, or CpH exhibit nonmonotonous behavior of reaction energies from Li to Cs. On the other hand, reaction energies *within* one group (the MX/HX set or MH/H_2 and MCH_3/CH_4 set) appear to be essentially independent of the metal. When M is in organometallic derivatives bound to carbon, two kinds of organoalkali-metal derivatives (σ vs $\sigma + \pi$ bonded) must be distinguished, due to their different electronic structure.

Our conclusions apply to the isolated gas-phase molecules. The effect of the inverted electronegativity of Li and Na may be reduced or even leveled out in aggregates or solvated complexes of slightly covalent compounds (e.g. alkyl alkali-metal compounds) in which larger contributions from metal p orbitals are expected. Further investigations will be necessary to assess these factors.

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Appendix

While the geometrical parameters of the calculated species are not the main topic of our paper, they are of interest, particularly in view of the lack of experimental as well as theoretical data for the complete series of the alkali-metal methides, amides, and cyclopentadienides.

The geometrical parameters of all species calculated are listed in Table V. At the HF level, the MH distances in MH are in good agreement with the experimental values for Li and Na[35] (Table Va). The calculated distances for K, Rb, and Cs are expected to be too long due to the neglect of core–valence correlation.[9b] The HF calculations overestimate the repulsion of metal-centered core ($n-1$ shell) electrons and ligand-centered valence electrons. Thus, the HF metal–ligand distances are too large. This artifact can be partially overcome by optimization with inclusion of electron correlation. Indeed, the MP2 MH distances are only slightly larger than the experimental ones. The influence of core–valence correlation on MH distances and the dissociation energies of alkali-metal hydrides has been discussed thoroughly by Fuentealba and Stoll[9b] and by Bauschlicher et al.[9e]

The geometries of the alkali-metal methides are shown in Table Vb. Again, metal–ligand distances are shortened (by ca. 3 pm) at the MP2 level for KCH_3, $RbCH_3$, and $CsCH_3$. The MCH angles decrease from Li to Na and increase from Na to Cs. This behavior reflects the decrease of ionicity from Li to Na (see Table I) and the increase from Na to Cs in the methides. Due to the large MC distance, the methyl unit in methylcesium is more ionlike than the other methyl compounds. Thus, it is more pyramidalized than for the other methides.

Table V. Geometries (d in Å, α and θ in deg) of MX (M = Li–Cs; X = H, CH_3, NH_2, OH, F, Cp) at the HF Level (Li–Cs) and the MP2(FU) Level (K–Cs)[a]

(a) MH ($C_{\infty v}$)

		Li	Na	K	Rb	Cs
d(MH)	HF	1.626	1.917	2.313	2.475	2.589
	MP2(FU)	(1.622)^{i}	(1.906)^{i}	2.255	2.413	2.528
	exptl^{b}	1.5957	1.8874	2.242	2.367	2.4938

(b) MCH_3 (C_{3v})

		Li	Na	K	Rb	Cs
d(MC)	HF	2.002	2.343	2.731	2.894	2.987
	MP2(FU)	(2.004)^{i}	(2.343)^{i}	2.698	2.859	2.956
d(CH)	HF	1.090 (1.094)^{i}	1.087 (1.091)^{i}	1.091	1.092	1.094
α(MCH)	HF	112.3 (111.6)^{i}	111.0 (110.0)^{i}	112.4	112.4	112.8

(c) MNH_2 (C_{2v})

		Li	Na	K	Rb	Cs
d(MN)	HF	1.753	2.107	2.434	2.589	2.675
	MP2(FU)	(1.755)^{i}	(2.120)^{i}	2.428	2.585	2.668
d(NH)	HF	1.000 (1.015)^{i}	1.001 (1.017)^{i}	1.003	1.004	1.004
α(MNH)	HF	127.4 (127.6)^{i}	127.8 (127.7)^{i}	128.3	128.3	128.2

(d) MOH ($C_{\infty v}$)

		Li	Na	K	Rb	Cs
d(MO)	HF	1.597	1.950	2.248	2.396	2.482
	MP2(FU)	(1.597)^{i}	(1.949)^{i}	2.250	2.402	2.486
	exptl	1.58^{c}	1.95^{d}	2.196^{e}	2.301^{f}	2.391^{f}
	HF^{g}	1.576	1.940	2.235	2.349	2.448
	CI(SD)^{g}	1.573	1.932	2.208	2.323	2.419
d(OH)	HF	0.931 (0.956)^{i}	0.933 (0.959)^{i}	0.935	0.936	0.937

(e) MF ($C_{\infty v}$)

		Li	Na	K	Rb	Cs
d(MF)	HF	1.588	1.933	2.222	2.367	2.448
	MP2 (full)	(1.588)^{i}	(1.945)^{i}	2.228	2.378	2.456
	exptl^{b}	1.564	1.926	2.172	2.270	2.345

(f) MCp (C_{5v})

		Li	Na	K	Rb	Cs
d(M–ring)	HF	1.784	2.248	2.649	2.835	2.978
	MP2 (full)	(1.747)^{j}	(2.213)^{k}	2.556	2.740	2.884
d(CC)	HF	1.405	1.405 (1.422)^{k}	1.403	1.402	1.401
d(CH)	HF	1.071	1.073 (1.086)^{k}	1.074	1.074	1.074
θ^{h}	HF	1.7	3.2 (3.5)^{k}	3.1	3.0	2.7

[a] 1-ve-cep's are given for Li, Na; 9-ve-ecp's are given for K–Cs; 4-, 5-, 6-, and 7-ve-ecp's are given for C, N, O, F. Basis set contraction scheme: Li, Na (211/31/1); K–Cs (21111/21111/11); C, N, O, F (311/311/1); H (311/11); for MCp C (31/31/1) H (31). [b] Reference 34. [c] Reference 35. [d] Reference 36. [e] Reference 37. [f] Reference 38. [g] Reference 9e. [h] Angle between the CH bond and the ring plane. The hydrogens are bent away from the metal. [i] All-electron calculations (MP2(FU)/6-31+G**) from ref 39. [j] Li–ring distance optimization at the MP2 level from ref 40. [k] All-electron calculation at the MP2(FU) level; 6-311G* basis sets for C and H, McLean/Chandler[41] basis set for Na.

The metal–ligand distances for the heavier alkali-metal hydroxides are again too long (about 4–10 pm) compared to the experimental values (see Tablve Vd). MP2 optimization of the MO distances does not change the results significantly. Apparently, our calculations do not adequately simulate dynamic *and* static polarization in these

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species. This is supported by the results of Bauschlicher et al.[9e] Their all-electron calculations near the HF limit resulted in distances only 3–6 pm longer than the experimental ones. CI(SD) optimizations only reduced the distances by about 2–3 pm.

The same problems arise for the alkali-metal amides (Table Vc). The MP2 MN distances are only slightly shorter than the HF values. Unfortunately, there are neither experimental nor high-level computationsl reference values. In view of the results for the alkali-metal hydroxides, we expect the MN separations to be overestimated by ca. 5 pm for KNH_2 and by ca. 10 pm for $RbNH_2$ and $CsNH_2$. The HF MNH angles follow the polarity of the MN bond. Thus, the widest MNH angle is observed for the most ionic MN bond (128.3°, $RbNH_2$) (cf. Table I). The HMH angle in $RbNH_2$ (103.4°) is close to the value for the free NH_2^- anion (103.2°).

The geometries of the alkali-metal fluorides (Table Ve) exhibit the same behavior as those of the hydroxides. Again, the MX distances are well described at the HF level for Li and Na. For K to Cs, the MF distances are too long by ca. 5–10 pm compared to high-level ab initio and experimental values.[9d,35] This is not improved at the correlated level.

The large correlation effects on the geometries of the heavier alkali-metal cyclopentadienides (Table Vf) will be discussed in detail elsewhere.[11] MP2 optimization reduces the K–, Rb–, and Cs–ring distances by about 9–10 pm. No experimental geometries are available for the alkali-metal cyclopentadienides, but we estimate the true equilibrium M–Cp distances to be still considerably shorter (by ca. 5–10 pm) than the MP2 results.

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