The Relationship between the Energies of Carbanions, R⁻, and their Lithiated Counterparts, RLi. An *Ab Initio* Study

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Summary While the methyl stabilisation energies of fifteen C_1—C_3 organolithium compounds, RLi, reflect (attentuation factor = 0·71) the methyl stabilisation energies of the corresponding anions, R^-, deviations are found when the degree of charge localisation or delocalisation is changed significantly by association with lithium.

Carbanions, perhaps the synthetically most useful reactive intermediates, are seldom free of counter-ion influences.[1] Nevertheless, it is common to equate a Grignard (RMgX) or lithium (RLi) reagent with the equivalent anion (R^-). To what extent is this simplification accurate? How does the presence of the metal influence the energies of an anionic system? Such questions are difficult to answer experimentally. Although the energies of many carbanions as isolated species in the gas phase[2] are now known accurately, the same is not true for their organometallic counterparts. The association of lithium compounds in the gas phase and in solution[3] complicates the determination of their energies.[4] Consequently, we have used *ab initio* molecular orbital theory to compare monomeric lithium compounds, RLi, with free carbanions, R^-.

We first consider the results with the entire set of fifteen C_1, C_2, and C_3 carbanions (Table) and their lithiated counterparts. All these species correspond to minima on their respective potential energy surfaces. Most of these systems

TABLE. Stabilisation energies (in kcal mol^{-1}).

RLi	Equation (1)[a]	Equation (2)[b]
H_3CLi	0·0	0·0
$HC{\equiv}CLi$	−47·9	−33·3, −33·9[c], −32·8[d]
$H_2C{=}CHLi$	−9·7	−4·8, −5·9[c], −6·0[e]
H_3CCH_2Li	5·6	5·0, 4·8[c]
$H_3CC{\equiv}CLi$	−40·3	−31·2
Allenyl-lithium	−33·5	−21·5
Allyl-lithium	−28·0	−15·7, −18·0[f], −17·1[e]
cis-1-Lithiopropene	−9·3	−4·0, −6·2[e]
trans-1-Lithiopropene	−7·4	−4·0, −6·1[e]
2-Lithiopropene	−10·5	−2·3, −4·0[e]
1-Lithiocyclopropene	−35·2	−21·0
3-Lithiocyclopropene	5·5	6·0
Cyclopropyl-lithium	1·8	2·1, 0·4[e]
Isopropyl-lithium	5·8	8·3, 6·2[e]
n-Propyl-lithium	2·7	4·0
$LiCH_2BH_2$	−54·7, −58·0[g]	−26·3[f], −24·1[h], −30·5[i]
$LiCH_2NH_2$	+1·9, +0·6[g]	−16·0[f], −5·7[h], −8·2[i]

[a] 4−31+G//4−31+G unless otherwise noted. [b] 4−31G//4−31G unless otherwise noted. [c] 6−31G*//4−31G. [d] MP2/6−31G*//4−31G. [e] MP2/4−31G//4−31G. [f] 3−21G//3−21G. [g] MP2/4−31+G//4−31+G. [h] 6−31G*//3−21G. [i] MP2/6−31G*//3−21G.

are 'classical' in that the lithium does not occupy a bridging position and the anion is largely associated with a single centre. However, the delocalised allyl and allenyl anions are also included. Allyl-lithium is symmetrically bridged[5] and allenyl-lithium has a similar structure.[6] The energetic relationships are analysed in terms of methyl stabilisation energies, defined by the isodesmic reaction (1) for the anions and reaction (2) for the lithium compounds. Reactions (1)

$$CH_3^- + RH \rightarrow CH_4 + R^- \qquad (1)$$

$$CH_3Li + RH \rightarrow CH_4 + RLi \qquad (2)$$

and (2) have been evaluated at somewhat different theoretical levels. The anions are calculated using the efficient 4-31+G basis, which includes a set of diffuse s and p functions on all non-hydrogen atoms.[7] Such diffuse functions are critically important for the accurate evaluation of anion energies,[7] but they do not affect the relative energies of the lithium compounds significantly.[8] Hence the 4-31G (5-21G for Li) basis has been used for the RLi species.[9] Both the anions and the lithium compounds were fully optimised. As indicated by the results in the Table, methyl stabilisation energies are often relatively insensitive to the inclusion of d-orbitals (polarisation functions) in the basis set (6-31G*)[10] or the effects of electron correlation (second order Møller–Plesset perturbation theory, MP2).[11] An important exception is $LiCH_2NH_2$, for which the inclusion of d-orbitals lowers the stabilisation energy considerably. This is due to the relatively poor description of electron-rich heteroatoms given by small split-valence basis sets.

The Figure demonstrates the close relationship between the relative carbanion energies and those of the corresponding lithium compounds. All fifteen points define a straight line with slope 0·71.† This result is very gratifying since it indicates that the monomeric organolithium compounds should reflect the energies of the corresponding anions proportionately. An attenuation is present, but the factor is relatively large. The common practice, to equate an anion with the corresponding lithium compound, is valid in these instances.

However, we have found notable exceptions to this generalisation. These exceptions fall into two categories. Some systems are *destabilised* by lithiation: the methyl stabilisation energies are less than 0·71 of the corresponding anions. Other systems are specifically *stabilised* by association with lithium: the methyl stabilisation energies often exceed those of the anion. We have discovered many instances of both types of behaviour; single examples of each are shown in the Figure for illustration.

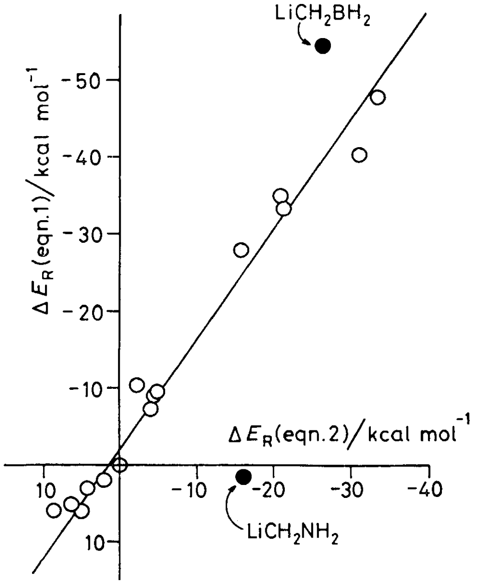

FIGURE. Anion stabilisation energies (4−31+G//4−31+G) *vs.* organolithium stabilisation energies (4−31G//4−31G). The line is that obtained from a linear regression analysis of the points marked by open circles.

The anionic charge in $CH_2BH_2^-$ is delocalised in an ethylene-like π-orbital; a very large methyl stabilisation energy, 55 kcal mol^{-1},‡ results.[12] The corresponding lithium compound, $LiCH_2BH_2$, is thus expected to have a methyl stabilisation energy of 0·71 × 55 = 39 kcal mol^{-1}. Instead, a much smaller value, 25 kcal mol^{-1}, is found. Association of the $CH_2BH_2^-$ anion with Li^+ results in charge *localisation*; lithium is bound more tightly to carbon than to boron. Such destabilisation due to charge localisation can be attributed to the partial covalent character of lithium bonds or to the relatively small size of the lithium cation. More ionic metals, like Na^+, should be more effective in developing anionic character.[13] A similar example of destabilisation through charge localisation is found in the LiO–CH=CH_2 form of the lithium enolate of acetaldehyde.[14]

$LiCH_2NH_2$ exemplifies the opposite influence.[15] The methyl stabilisation energy is considerably larger than the methyl stabilisation energy of $CH_2NH_2^-$ (shown by the deviation to the lower left in the Figure). In the anion,

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† A linear regression analysis of all points except those for $LiCH_2BH_2$ and $LiCH_2NH_2$ gives a slope of 0·7107, an intercept with the RLi axis of +1·8 kcal mol^{-1}, and a correlation coefficient of 0·9903.

‡ 1 cal = 4·184 J.

the negative charge is largely carbon-centred. However, the lowest-energy structure of $LiCH_2NH_2$ is nonclassical; lithium bridges between carbon and nitrogen. This association with two centres, in effect, delocalises the negative charge. Cyclic three-centre, four-electron bonding, possible because of the availability of vacant p-orbitals on lithium, affords an alternative explanation of the extra stabilisation. Other metals, like Na, are expected to be *less effective* in such instances.[13]

Three types of systems have thus been identified. When the negative charge in an anion and the lithium in the corresponding organometallic are largely associated with a single atom, or both are more or less symmetrically associated with more than one atom, the stabilisation energies correlate. The attenuation factor, 0·71 for lithium, should vary with the covalent character of the metal. Delocalised carbanions may be destabilised, on a relative basis, by association at only a single centre with a more covalent metal. Other localised carbanion systems may be stabilised by bridging lithium. This helps explain the origin of metal-specific effects. Metals more ionic than lithium may either be as effective, more effective, or less effective in stabilising an anionic system, depending on the nature of the species involved.

Under experimental conditions, *i.e.*, in condensed phases, lithium compounds are associated to different extents depending on structure, solvent, concentration, ligand, *etc.* Solvation energies are also variable. Our results on idealised isolated lithium species provide a basis for interpreting experimental thermochemical results. We are now investigating the dimerisation, association, and solvation of lithium compounds calculationally.

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