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# ESCA STUDIES OF CARBANIONIC COMPOUNDS: BUTYLLITHIUM IN HEPTANE SOLUTION AND DIBUTYLMERCURY IN THE GAS PHASE

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## ABSTRACT

Two organometallic reagents, butyllithium in heptane solution and dibutylmercury in the gas phase, have been studied by means of core electron spectroscopy. The property of particular interest was the charge polarization as reflected by the ESCA shifts. In the butyllithium compound the C1s binding energy is shifted to a lower value by 1·8 eV for C-1 (situated closest to the $Li^+$ ion) relative to the heptane solvent carbon. This is due to the anionic character of the C-1. The interpretation of the experiments was supported by comparing the results with *ab initio* calculations made on geometry-optimized butyllithium, butyl anion and butane.

## INTRODUCTION

Organometallic compounds are of great interest as reagents in organic synthesis and a knowledge of the nature of such compounds, especially in solution, is therefore very important. Electron spectroscopy offers a means of studying such systems and yields information on the charge distribution via the chemical shifts of the core levels. This paper reports the first investigation by liquid ESCA of an organometallic compound, butyllithium, together with a gas-phase investigation of dibutylmercury. The interpretation is supported by results of *ab initio* MO–LCAO–SCF calculations on butyllithium, butyl anion and butane.

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## EXPERIMENTAL AND CALCULATIONAL DETAILS

The basic principles for obtaining ESCA spectra from a liquid sample have been described previously.[1-3] The method is based on the creation of a thin liquid film on a stainless-steel trundle submerged in a cup containing the liquid sample. The cup is enclosed in a differentially pumped compartment in which the pressure is determined by the vapour pressure of the liquid sample (typically below 0·1 mbar). In the present investigation spectra from butyllithium in heptane solution were recorded at 179 K. At this temperature a small gas-phase contribution from the solvent was present in the spectra, which was taken into account when subsequently analysing the data. (Normally the gas signal is suppressed by applying a voltage between the trundle and the spectrometer entrance slit.[2] Owing to certain complications in the handling of the present sample, this procedure could not be used.) Owing to the high reactivity of butyllithium the sample had to be syringed into the sample compartment under a nitrogen atmosphere. The spectra from the gas-phase dibutylmercury were recorded without the trundle with the pure liquid compound in the sample compartment. This gave a sufficient vapour pressure at room temperature to yield intense spectral lines.

The calculations were carried out using the SCF program package MOLECULE–ALCHEMY. The basis sets were Dunning's and Hay's contractions of Huzinaga's Gaussian-type basis sets. An additional *d*-function with exponent 0·85 was added to the carbon basis set, together with an extra *p*-function with exponent 1·00 to the hydrogen basis set, resulting in the following basis sets: C, ⟨3s, 2p, 1d⟩; H, ⟨2s, 1p⟩; and Li, ⟨3s, 2p⟩.[4,5] The geometries

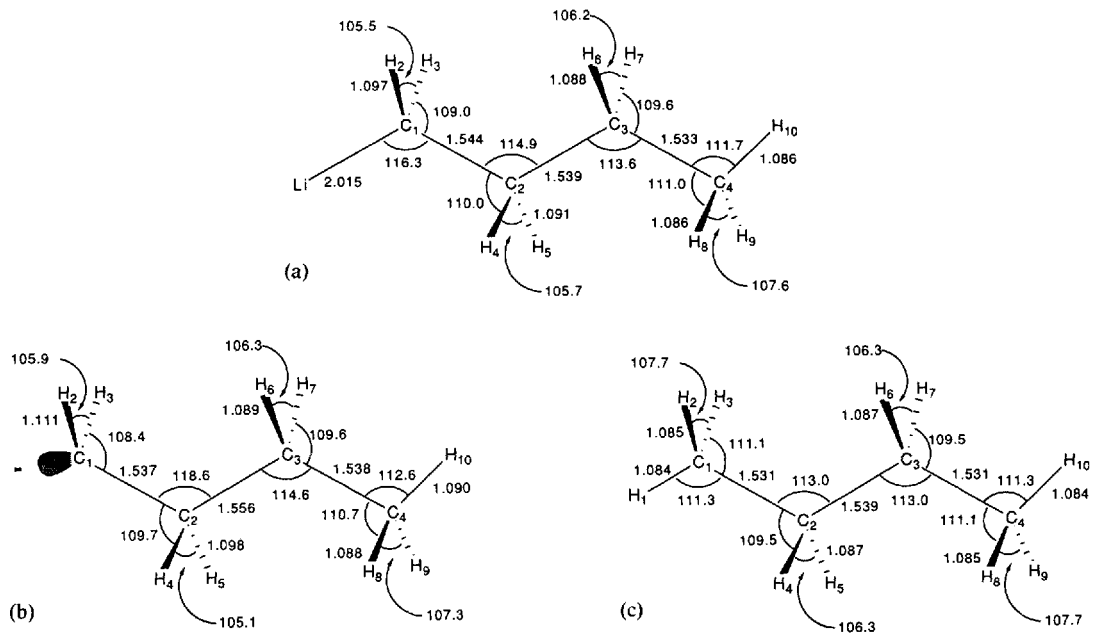


Figure 1. Optimized $C_s$ geometries within the 6-31G basis set for (a) butyllithium, (b) butyl anion and (c) butane. Bond lengths in ångströms and bond angles in degrees.

* The MOLECULE–ALCHEMY program package incorporates the MOLECULE integrals program written by J. Almlöf and the ALCHEMY program written by P. Bagus, B. Liu, M. Yoshimine and D. MacLean, and modified by P. Bagus and U. Wahlgren.

for the different molecular species were obtained from total optimizations with the 6-31G basis set[6,7] using the GAUSSIAN 82 program.* The only constraint in the geometry optimizations was that of $C_s$ symmetry. The optimized geometries are shown in Figure 1. Owing to the size of the systems, calculations were performed only on monomer forms. Experiments in solution[8] indicate the presence of a hexamer structure in hydrocarbon solvents. Our aim in this work, however, was to study the polarization effects between the metal ion and the hydrocarbon moiety as expressed by ESCA shifts. In this context we chose to focus on the monomers, although we did not exclude possible effects due to higher aggregate formation.

## RESULTS AND DISCUSSION

Figure 2 shows a typical spectrum from ca 1·6 M butyllithium in heptane. As mentioned above, the spectrum also includes a contribution from the gas phase of heptane. The solvent gas-phase signal appears as an asymmetry on the left-hand side of the C1s peak. The structure present on the right-hand side of the peak we assigned to the solute butyllithium. A 1.6 M solution of butyllithium in heptane implies that the signal ratio from a single butyl carbon atom to the other carbon atoms will be 0·031 : 1. We performed curve fitting to several C1s spectra using the program CRUNCH.† Three peaks were fitted: one solvent gas peak (left-hand peak), one main peak (consisting of the solvent liquid and a contribution from solute neutral carbons) and one solute peak (right-hand peak). From the fitting we found that the right-hand peak averaged 3·4% of the intensity of the main peak and was shifted 1·8 eV to lower binding energy. This shift is comparable to that found previously for methyllithium in the solid phase (2·4 eV referred to contaminant carbon).[9] The agreement between experiment and theoretical

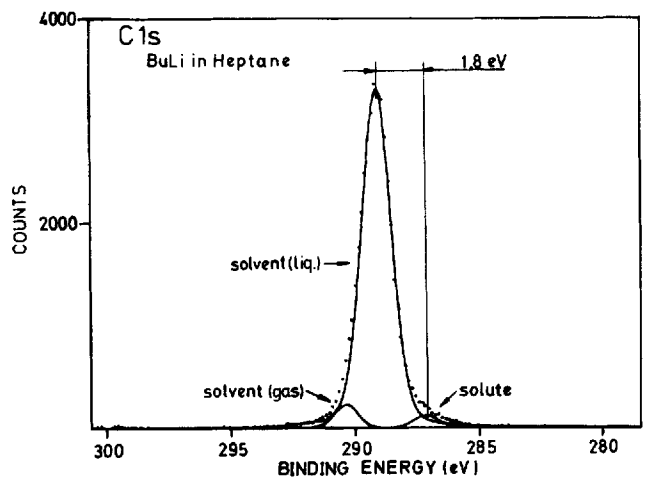


Figure 2. A typical C1s spectrum of butyllithium in heptane. Points correspond to experimental values. The solid curves were obtained from deconvolution (without preassumptions concerning relative peak heights, widths or positions). The right-hand peak represents 3·4% of the middle peak.

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Table 1. The 1s orbital energy, binding energy and relaxation energy for the butyllithium molecule, the butyl anion and the butane molecule[a]

| Species | Parameter | C-1 | Δ(4 − 1) | C-2 | Δ(4 − 2) | C-3 | Δ(4 − 3) | C-4 |
|---|---|---|---|---|---|---|---|---|
| Butyllithium molecule | $-\varepsilon_i$ | 302·6 | 1·7 | 304·1 | 0·2 | 304·2 | 0·1 | 304·3 |
| | $E_b$(1s) | 288.5 | 2.6 | 290.5 | 0.6 | 290.6 | 0.5 | 291.1 |
| | $E^{\text{Relax}}$ | 14.1 | | 13.6 | | 13.6 | | 13.2 |
| Butyl anion | $-\varepsilon_i$ | 297.0 | 4.2 | 299.6 | 1.6 | 300.4 | 0.8 | 301.2 |
| | $E_b$(1s) | 283.2 | 4.8 | 286.0 | 2.0 | 286.8 | 1.2 | 288.0 |
| | $E^{\text{Relax}}$ | 13.8 | | 13.6 | | 13.6 | | 13.2 |
| Butane molecule | $-\varepsilon_i$ | 305.0 | 0.0 | 305.2 | −0.2 | 305.2 | −0.2 | 305.0 |
| | $E_b$(1s) | 291.9 | 0.0 | 291.8 | 0.1 | 291.8 | 0.1 | 291.9 |
| | $E^{\text{Relax}}$ | 13.1 | | 13.4 | | 13.4 | | 13.1 |

[a] C-1 refers to the carbon atom lying closest to the lithium atom and the numbering is consecutive along the chain. The shifts with respect to C-4 are also given. The energies are given in eV.

predictions concerning both line shift and intensity leads to the interpretation that the right-hand peak is due to a single negatively charged carbon atom in the butyl anion. To substantiate this interpretation further the binding energy values obtained from our *ab initio* calculations are shown in Table 1. Both C1s orbital energies, binding energies, $E_b$ (1s) (i.e. the difference in total energy between the ground state and core hole state) and the relaxation energies (i.e. the difference between orbital energy and the binding energy) for the various sites are included. It should be noted that our experimental data refer to dissolved molecular species, which means that a solvent polarization shift lowers the binding energies by about 1·2–1·5 eV compared with the gas-phase values. The calculation predicts the binding energy to be approximately 2 eV smaller for C-1 than for the other atoms along the carbon chain. This shift is due primarily to the location of negative charge on C-1, as indicated by the Mulliken population analysis (cf. Table 2). [As pointed out by several workers (see e.g. Refs. 10–14), the Mulliken population analysis for C—Li bonds may lead to misinterpretations concerning covalency. However, this does not influence the interpretations in this paper, which are based on calculated ΔSCF C1s binding energies. Therefore, we restrict ourselves to qualitatively noting only trends in charge flow.] It is also interesting to note a difference in relaxation energy along the chain of 0·9 eV, which is probably due to a higher initial state charge density on C-1.

In order to elucidate further the interaction between the lithium ion and the butyl anion and the relationship to the chemical shifts, calculations were also performed on the uncomplexed butyl anion only. Two main effects can be noted on comparison with the BuLi compound. First, all energies are shifted to lower values by more than 3 eV. As can be seen from Table 2, the effect of the $Li^+$ ion on approach to the butyl anion results in a redistribution of Mulliken charge in the entire molecule. The main effect is a flow of charge from the hydrogens via the intermediate carbons towards the $Li^+$ ion. This, together with the electrostatic potential caused by the positive $Li^+$ ion, will result in an increase in the 1s binding energies for all the carbons in the BuLi compound. Second, a differential effect along the carbon chain also occurs owing to the presence of the $Li^+$ ion. This differential effect amounts to more than 2 eV, such that the calculated shift between C-1 and C-4 is 4·8 eV in the anion and only 2·6 eV in the BuLi compound (see Table 1). The experimental data confirm this action of the $Li^+$ ion on the butyl anion, since the shift for C-1 with respect to heptane solvent was found to be 1·8 eV, which is in reasonable agreement with the theoretical value of 2·6 eV (shift between heptane and C-4 in BuLi $\leqslant$ 0·3 eV, see below).

Table 2. The number of electrons from the Mulliken population analysis[a]

| Species | Li | C-1 | C-2 | C-3 | C-4 | H-1 | H-2,3 | H-4,5 | H-6,7 | H-8,9 | H-10 |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Butyllithium molecule | 2·469 | 6·702 | 6·021 | 6·123 | 6·352 | | 1·854 | 1·904 | 1·850 | 1·818 | 0·907 |
| | 2·156 | 7·012 | 5·883 | 6·157 | 6·338 | | 1·241 | 1·767 | 1·805 | 1·781 | 0·860 |
| | 2·311 | 6·564 | 6·498 | 5·984 | 6·345 | | 1·732 | 1·244 | 1·706 | 1·776 | 0·840 |
| | 2·315 | 6·714 | 5·903 | 6·605 | 6·172 | | 1·822 | 1·761 | 1·196 | 1·675 | 0·837 |
| | 2·353 | 6·709 | 6·062 | 5·971 | 6·854 | | 1·822 | 1·863 | 1·681 | 1·111 | 0·574 |
| Butyl anion | | 6·677 | 6·072 | 6·118 | 6·359 | | 2·103 | 1·994 | 1·899 | 1·836 | 0·942 |
| | | 6·878 | 5·865 | 6·159 | 6·340 | | 1·394 | 1·833 | 1·846 | 1·794 | 0·891 |
| | | 6·449 | 6·574 | 5·968 | 6·354 | | 1·952 | 1·291 | 1·750 | 1·792 | 0·870 |
| | | 6·536 | 6·024 | 6·602 | 6·170 | | 2·041 | 1·828 | 1·236 | 1·694 | 0·869 |
| | | 6·575 | 6·121 | 6·016 | 6·849 | | 2·043 | 1·944 | 1·722 | 1·130 | 0·600 |
| Butane molecule | | 6·344 | 6·117 | 6·117 | 6·344 | 0·897 | 1·803 | 1·839 | 1·839 | 1·083 | 0·897 |
| | | 6·852 | 5·944 | 6·150 | 6·332 | 0·564 | 1·095 | 1·668 | 1·785 | 1·762 | 0·848 |
| | | 6·168 | 6·584 | 5·978 | 6·337 | 0·825 | 1·657 | 1·182 | 1·684 | 1·757 | 0·828 |
| | | 6·337 | 5·978 | 6·584 | 6·168 | 0·828 | 1·757 | 1·684 | 1·182 | 1·657 | 0·825 |
| | | 6·332 | 6·150 | 5·944 | 6·852 | 0·848 | 1·762 | 1·785 | 1·668 | 1·095 | 0·564 |

[a] For each of the molecular species the first row represents the neutral species and the following four rows represent the case when the atoms C-1, C-2, C-3 and C-4 respectively, are ionized.

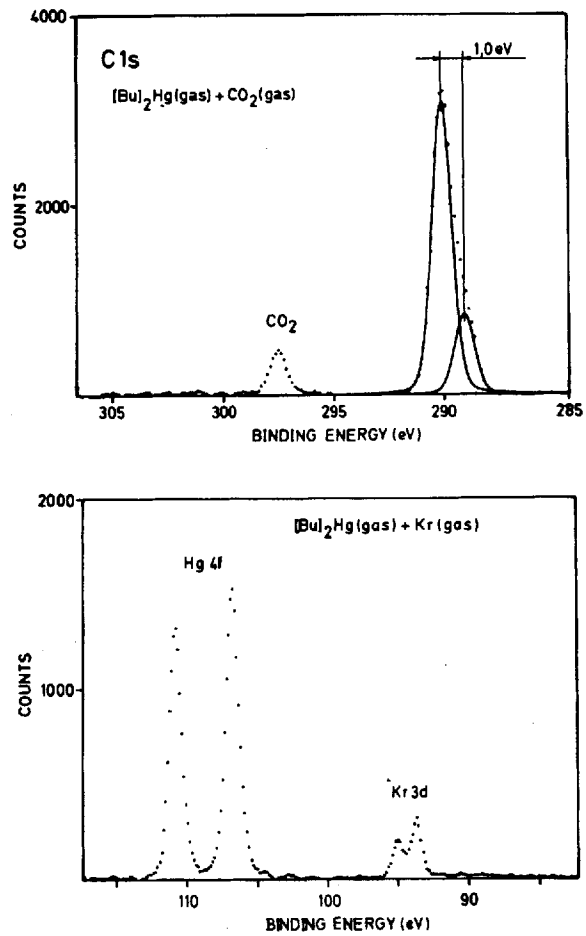


Figure 3. The upper spectrum shows the C1s peaks from dibutylmercury in the gas phase together with a carbon dioxide C1s calibration peak. Points correspond to experimental values. The solid curves were obtained from deconvolution (without preassumptions). The lower spectrum shows the Hg4f lines from dibutylmercury in the gas phase. The $Hg4f_{7/2}$ line (right) was determined to $E_b = 106{\cdot}7$ eV. The spectrum also includes the Kr3d line of the krypton gas calibrant simultaneously present.

Turning next to dibutylmercury, Figure 3 shows the C1s and the Hg4f spectra obtained in gas-phase measurements. Here, the C1s spectrum of the butyl moiety is clearly resolved into two components with an intensity ratio of ca 3 : 1 (there is not, of course, any heptane solvent peak present in this spectrum; see Figure 3). The shift found between the components is $\Delta E_b = 1{\cdot}0$ eV, which is significantly smaller than that for BuLi ($\Delta E_b = 1{\cdot}8$ eV). It should be borne in mind that the C1s spectrum for BuLi in heptane does not allow the explicit resolution of the C1s components of the solute owing to overlap with the solvent peak (cf. Figure 2). However, it is unlikely that the shift between the solvent peak and the second non-observed solute peak is as large as 0·8 eV (the calculated shifts with respect to butane as given in Table 1 are therefore probably overestimated). One strong argument for this conclusion can be derived from the dibutylmercury spectrum, where it can be noted that the major C1s peak has only a small shift with respect to heptane in the gas phase ($\Delta E = 0{\cdot}3$ eV; 290·0 eV vs

290·26 eV[15]). The substituent effect between dibutylmercury and butyllithium is not likely to be as large as 0·5 eV (0·5 eV = 0·8–0·3 eV) for the carbon most remote from the substitution. In fact, the most probable effect on substitution from mercury to lithium is a combined shift of the C1s levels of the butyl anion. Hence, in analogy with the comparison between the pure anion and the BuLi compound, the C1s level of the carbon atom closest to the lithium ion will shift more than the C1s levels in the other three carbon atoms. Hence, the larger shift observed between the peaks in the BuLi spectrum is probably also representative of a larger separation between the C1s levels in the butyl group for the lithium case than for the mercury case (1·8 eV vs 1·0 eV would be an upper bound to the difference). This is in line with the stronger ionic character expected for the BuLi compound.

Concerning finally the $Hg4f_{7/2}$ binding energy, it can be noted that the value obtained for dibutylmercury lies below the atomic value [$E_b$(dibutylmercury) = 106·7 eV vs $E_b$(atom) = 107·06 eV[16]]. This seems surprising since a charge transfer occurs from the metal atom to the butyl ligands, hence a shift in the positive direction would be expected for the metal levels. However, the shift between the two cases is probably the net result of three counteracting effects, the contraction of the metal atom charge density between the free atom and the compound (leading to a negative shift), a higher relaxation energy for the compound than for the atom (also leading to a negative shift) and the charge transfer (leading to a positive shift). For this compound the first two effects are apparently the dominating contributions to the shift.

Our further studies will proceed to other lithium systems and also other organometallic systems whose charge distribution is expected to be different from both of the cases studied here.

## CONCLUSION

We have studied two organometallic compounds, the butyl compounds of lithium and mercury. For butyllithium the main result is a major binding energy shift of the C1s energy level of the carbon atom situated closest to the $Li^+$ ion. The calculations show that the $Li^+$ ion causes a differential shift in the energies of the carbon atoms in the butyl anion chain. This is also apparent with dibutylmercury, where the effect is estimated to be smaller than for butyllithium. The combined use of our photoelectron experiments in the gas and liquid phases and theoretical calculations show that information pertaining to the charge distribution within the carbanion can be extracted.

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