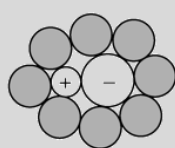
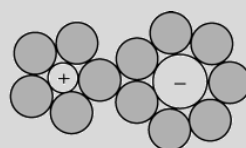


# Ion Pairing and s-Block Reagents

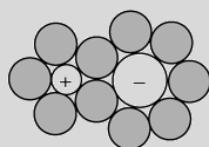
Models/Topics Covered: Ion Pairing/Association, Electrostatics, Redox, HSAB Theory, Acidity, Solution-Phase Behaviour, Heteronuclear NMR, Raman, VSEPR



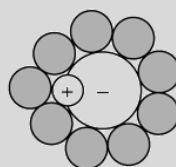
contact ion pair



solvent-separated ion pair



solvent-shared ion pair



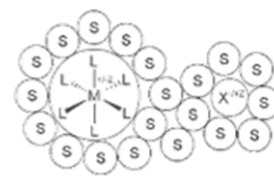
penetrated ion pair

Types of Ion Pairing: Contact Ion Pair (CIP), Solvent-Separated Ion Pair (SSIP), Solvent-Shared Ion Pair (SIP), and Penetrated Ion Pair. Reproduced from Ref[3] (Scheme 1)

## Question 1 (Ion Pairing/Association)

Ion pairing has implications for the kinetics of organic and inorganic reactions, as well as physical processes, including crystallisation from supersaturated solutions. The following questions focus on factors affecting ion pairing and the potential implications of association behaviour for reactivity.

- (i). Indicate the type of ion-pairing shown by the following species:



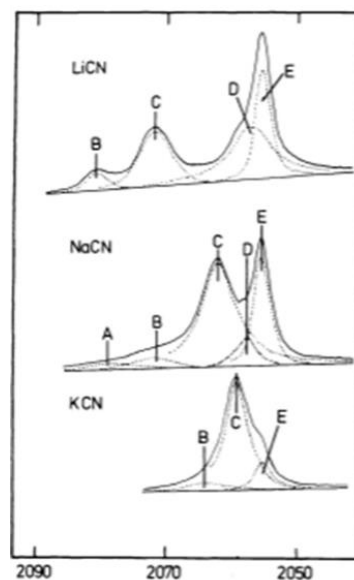
- (ii). Which case is more likely to be a contact ion pair in the following examples?

- NaCl in aqueous solution or NaCl in methanolic solution
- $\text{MgSO}_4$  in seawater or NaCl in seawater
- CsCl in aqueous solution or CsI in aqueous solution
- 0.5 mol/kg CsCl aqueous solutions or an 11 mol/kg CsCl aqueous solution
- LiCN in liquid ammonia or  $\text{Al}(\text{CN})_3$  in liquid ammonia

- (iii). Raman data (see right) shows the peaks in the  $\nu(\text{CN})$  region for a series of alkali metal cyanides. Indicate why multiple peaks are present. Peak E appears at the same position in each spectrum, what might this indicate about its assignment?

- (iv). The degree of formation of contact ion pairs in ammoniacal solutions of alkali metal cyanides, thiocyanides, azides, and nitrates increases in an unexpected order:  $\text{Li(I)} < \text{Na(I)} < \text{K(I)} < \text{Rb(I)} < \text{Cs(I)}$  (where measurement is possible). Give a potential reason for this.

- (v). For the single site Ziegler-Natta Polymerisation of ethylene, the generated catalyst  $[\text{L}_2\text{ZrMe}][\text{MeB}(\text{C}_6\text{F}_5)_3]$  is  $10^5$  times less active than  $[\text{L}_2\text{ZrMe}][\text{MeB}(2\text{-C}_6\text{F}_5\text{C}_6\text{F}_4)_3]$  (where L = Cp-derived ligands). Explain why, and indicate how the rate of the slower reaction might be increased.

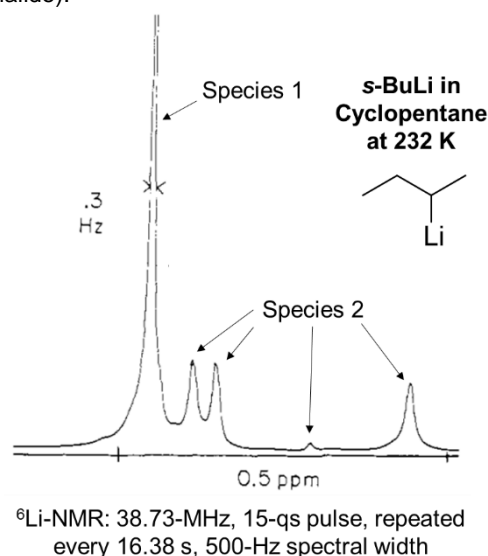
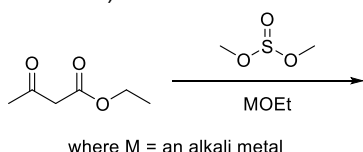


The  $\nu(\text{CN})$  region of the Raman spectra of cyanide solutions in liquid ammonia at 298 K

## Question 2 (Organolithium Compounds)

Explain the following observations:

- Combining MeLi with CuI in THF at -78 °C forms a new species. This species is not formed in any reasonable quantity through an analogous process to direct synthesis of MeLi (Li metal + alkyl halide).
- The new species indicated in part (i) has very different reactivity to MeLi. It does not react with cyclohexanone, although MeLi does, and will undergo clean S<sub>N</sub>2 substitution reactions with alkyl halides, although MeLi does not.
- n*-BuLi in an anhydrous THF solution rapidly degrades if the temperature is raised above 0 °C. Three products are formed, two are gaseous.
- The rate of O-alkylation versus C-alkylation for the reaction below is much lower when the alkali metal used is Li rather than K. O-alkylation rate is also higher in HMPA than in DMF (specifically when Na is used, but should follow for Li and K).



- The <sup>6</sup>Li-NMR spectrum of sec-butyllithium in cyclopentane at -41 °C (see right) contains evidence of multiple species. One of those species gives multiple signals.

## Question 3 (Grignard Reagents)

The following questions aim to build up a relatively complete view of the complex system generated during the Grignard reaction. A proposed mechanism for Grignard reagent generation is included for your reference.

- MeMgBr is stabilised in diethyl ether and THF, but degrades in dioxane. Draw the structures formed in each of these cases.
- Grignard reagent formation is promoted by vigorously stirring the dry magnesium metal turnings prior to the introduction of solvent and reagents, and by the presence of I<sub>2</sub> (or MgI<sub>2</sub>). Explain these observations.
- Provide a mechanism for the reaction of the Grignard reagent *i*PrMgBr with ethyl acetate.
- What are the two common side products produced during a Grignard Reaction? (Note: these can be minimised through reaction optimisation so are not always observed).



Numerous possible mechanisms have been proposed for Grignard formation. This is an example favoured by Ref[12]

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