

GAS PHASE REACTIONS OF NEGATIVE IONS

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- Why has the study of the gas phase ion/molecule reactions of negative ions lagged so far behind the gas phase ion/molecule reactions of positive ions?
- Has the production of negative ions been an impediment?
- Are negative ions less stable than positive ions?
- Are negative ions less reactive than positive ions?
- What properties of a negative ion might confer reactivity or non-reactivity?
- What kinds of molecules react with negative ions?

1. Almost all commonly used ionization methods can produce both positive and negative ions but there are problem areas, many metal M^+ ions but few M^- ions.

2. Anions with high electron affinities will be stable. Tandem mass spectrometry can probe the stability of ions but some anions simply lose an electron (frustrating the mass spectrometrists). The structures of anions may hold the key to their stability and reactivity, and now density functional calculations allow us to investigate anion, neutral and positive ion structures.

3. There are few comparative studies of similar anions and cations but if we use the examples of the carbon ions, then the positive ions are more reactive than the anions.

4. Some of our work with transition metal containing anions shows that the structure of the anion is important in both stability and reactivity. Reactivity is enhanced by the exposure of reactive sites. Non-reactivity or reduced reactivity can occur by hiding potentially reactive sites in the ion and/or hiding or distributing the charge.

5. Many different molecules with a variety of properties, molecular shapes and sizes eg. S_8 , P_4 , CH_3OH , may react with negative ions.

In trying to answer/rationalize these questions (and others not posed above) examples from our work and the work of others will be used. As an example, our study of the reactions of transition metal sulfide anions with P_4 show some interesting reactivity and structural effects by changing the metal from copper to nickel.

The calculated structures of (a) $[Ni_2S_2P_4]^-$ and (b) $[Cu_2S_2P_4]^-$ are shown below with the copper ion showing the insertion of a P_2 unit into a copper sulfur bond.

