

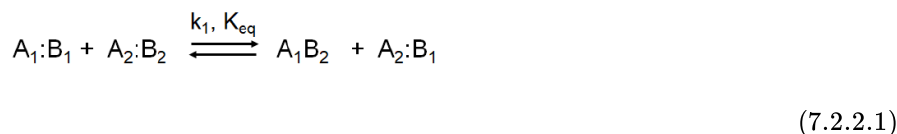
7.2.2: Applications of Hard Soft Acid Base Theory

The Hard-Soft acid-base principle (HSAB Principle) explains patterns in Lewis acid-base reactivity in terms of a *like reacts with like preference*. Both thermodynamically and kinetically hard acids prefer hard bases and soft acids soft bases. Specifically,

- Thermodynamically, hard acids form stronger acid-base complexes with hard bases while soft acids form stronger complexes with soft bases.
- Kinetically, hard acids/electrophiles react more quickly with hard bases/nucleophiles while soft acids/electrophiles react more quickly with soft bases/neucleophiles

Applications of the HSAB principle include

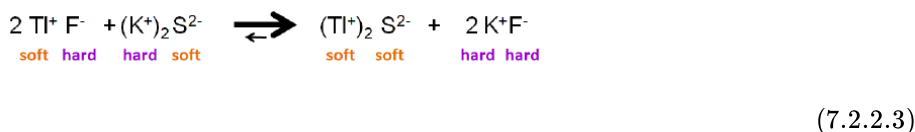
1. Predicting the equilibrium or speed of *Lewis acid-base metathesis and displacement reactions*. In a Lewis acid-base *metathesis reaction* the acids and bases swap partners



For example, the equilibrium position of the metathesis reaction between TlF and K₂S favors the products:



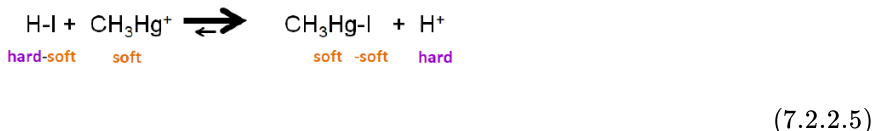
consistent with the HSAB's hard-hard and soft-soft preference.



The HSAB principle also allows for prediction of the position of displacement reactions, in which a Lewis acid or base forms an adduct using a base or acid from an existing Lewis acid-base complex. In these reactions, the displacement of acid or base from the reactant complex to may be thought of as a sort of metathesis reaction, one in which in the unbound acid or base switches places with one in the complex. For example, the reaction between HI and methylmercury cation

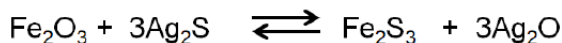


involves displacement of an iodide from HI to give CH₃HgI. The position of the equilibrium favors CH₃HgI since both CH₃Hg⁺ and I⁻ are both soft, while H⁺ is a hard acid.



? Exercise 7.2.2.2

Predict the position of equilibrium for the following reaction.



Answer

The equilibrium will favor the reactants ($K < 1$) since the hard-hard and soft-soft interactions in the reactants are more stable than the hard-soft interactions in the products.



? Exercise 7.2.2.3

Predict whether K for the following equilibria will be $\ll 1$, ~ 1 , or $\gg 1$.

- $2\text{HF} + (\text{CH}_3\text{Hg})_2\text{S} \rightleftharpoons 2\text{CH}_3\text{HgF} + \text{H}_2\text{S}$
- $\text{Ag}(\text{NH}_3)_2^+ + 2\text{PH}_3 \rightleftharpoons \text{Ag}(\text{PH}_3)_2^+ + 2\text{NH}_3$
- $\text{Ag}(\text{PH}_3)_2^+ + 2\text{H}_3\text{B}-\text{SH}_2 \rightleftharpoons 2\text{H}_3\text{B}-\text{PH}_3 + \text{Ag}(\text{SH}_2)_2^+$
- $\text{H}_3\text{B}-\text{NH}_3 + \text{F}_3\text{B}-\text{SH}_2 \rightleftharpoons \text{H}_3\text{B}-\text{SH}_2 + \text{F}_3\text{B}-\text{NH}_3$

Answer

- $K \ll 1$ since the reactant adducts are hard-hard and soft-soft while the products involve hard-soft interactions
- $K \gg 1$ since the reactant complex, diamine silver(I) is a complex of a hard base, NH_3 , with the soft acid, Ag^+ , while the product is a complex of the same soft acid with the soft base phosphine.
- $K \sim 1$ since all the adducts amongst the reactants and products involve soft acids and bases
- $K \gg 1$ since BH_3 is a softer acid than BF_3 so it will form a stronger complex with the softer base H_2S while the harder BF_3 forms a stronger complex with the harder base NH_3 .

2. Predicting the relative strengths of a given set of *Lewis acids or bases towards a particular substrate*. Consider, for example, the relative strengths of a BH_3 , BMe_3 , and BF_3 towards group 15 hydrides like NH_3 , PH_3 , and AsH_3 . Of the boranes listed, the hardest acid BF_3 is the strongest acid towards the hard base NH_3 while BH_3 is the strongest towards AsH_3 .[†]

? Exercise 7.2.2.4

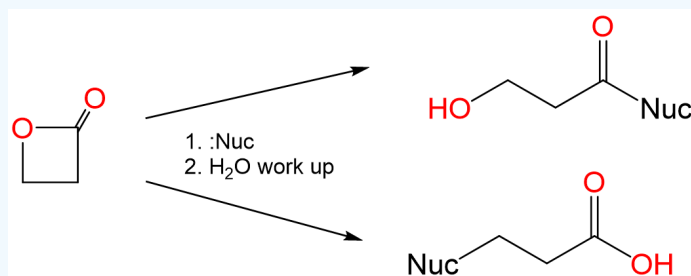
Which acid will form the most stable complex with CO - BH_3 , BF_3 , or BMe_3 ?

Answer

BH_3 . Since CO forms complexes primarily through its carbon lone pair it is a soft base and so will form the strongest complex with the softest Lewis acid.

? Exercise 7.2.2.5

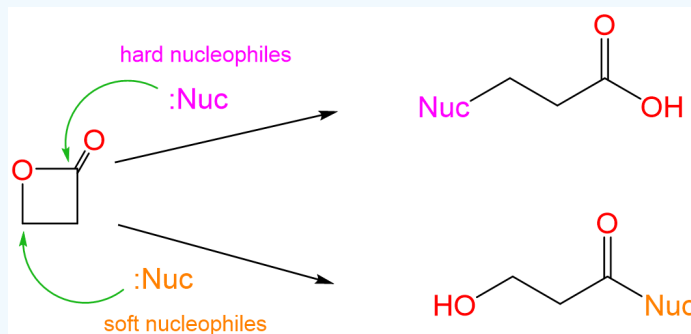
When lactones react with nucleophiles they can undergo ring opening reactions to give either an alcohol or carboxylic acid, as shown for propiolactone below:



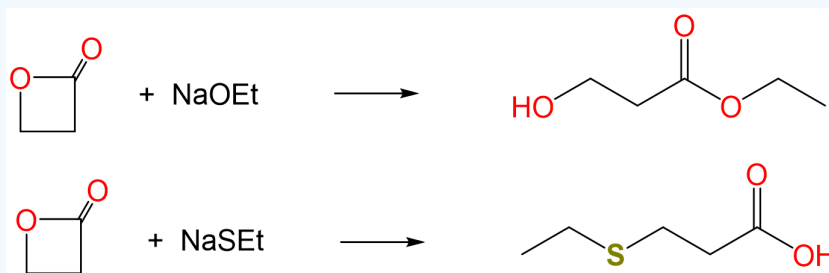
In the reaction above, sterically unhindered alkoxides give one product and sterically unhindered thioalkoxides the other. Explain why this is the case and predict the products of the reaction between propiolactone and the sodium salts of ethoxide and thioethoxide.

Answer

The two reaction products correspond to nucleophilic attack at the lactones two electrophilic carbon centers. Specifically, the acid is produced by attack at the softer C^I center of the CH_2 directly attached to the ester oxygen and the alcohol by nucleophilic attack at the harder C^{III} center of the ester carbonyl.



Consequently, it is reasonable to expect that the harder base ethoxide will nucleophilically attack the harder carbonyl carbon while the softer thioethoxide will attack the softer methylene carbon.



Notes

* Despite the fruitfulness of this observation, in general it is important to reduce the potential for observer bias by checking observations like these against compounds reported in the chemical literature and databases like the Inorganic Crystal Structure and Cambridge Crystallographic Databases.

** These are very soluble in water, to the point where some solutions are perhaps better described as solutions of water in the halide.

† This can be predicted based on the relative hardness of BF_3 , BR_3 , and BH_3 in the list of hard and soft acids. However, for those of you who may be confused as to why H is considered a better electron donor for the purposes of softening a Lewis acid center while alkyl groups are better electron donors for the purposes of stabilizing carbocations in organic chemistry, the dominant effect is the lower electronegativity of H relative to carbon (in CH_3). The effect of electron donation due to hyperconjugation isn't as great for thermodynamically stable bases like BX_3/BR_3 .

References

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2. Pearson, R. G., Hard and Soft Acids and Bases. Journal of the American Chemical Society 1963, 85 (22), 3533-3539.
3. Fleming, I., Molecular orbitals and organic chemical reactions. Reference ed.; Wiley: Hoboken, N.J., 2010.

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