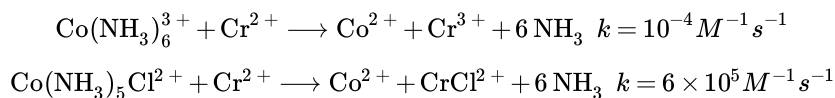


9.2.2: Inner Sphere Electron Transfer

In some cases, electron transfers occur much more quickly in the presence of certain ligands. For example, compare the rate constants for the following two electron transfer reactions, involving almost exactly the same complexes:



(Note: aqua ligands are omitted for simplicity. Ions, unless noted otherwise, are aqua complexes.)

Notice two things: first, when there is a chloride ligand involved, the reaction is much faster. Second, after the reaction, the chloride ligand has been transferred to the chromium ion. Possibly, those two events are part of the same phenomenon.

Similar rate enhancements have been reported for reactions in which other halide ligands are involved in the coordination sphere of one of the metals.

In the 1960's, Henry Taube of Stanford University proposed that halides (and other ligands) may promote electron transfer via bridging effects. What he meant was that the chloride ion could use one of its additional lone pairs to bind to the chromium ion. It would then be bound to both metals at the same time, forming a bridge between them. Perhaps the chloride could act as a conduit for electron transfer. The chloride might then remain attached to the chromium, to which it had already formed a bond, leaving the cobalt behind.

Electron transfers that occur via ligands shared by the two metals undergoing oxidation and reduction are termed "inner sphere" electron transfers. Taube was awarded the Nobel Prize in chemistry in 1983; the award was based on his work on the mechanism of electron transfer reactions.

? Exercise 9.2.2.1

Take another look at the two electron transfer reactions involving the cobalt and chromium ion, above.

- What geometry is adopted by these complexes?
- Are these species high spin or low spin?
- Draw d orbital splitting diagrams for each complex.
- Explain why electron transfer is accompanied by loss of the ammonia ligands from the cobalt complex.
- The chloride is lost from the cobalt complex after electron transfer. Why does it remain on the chromium?

Answer a

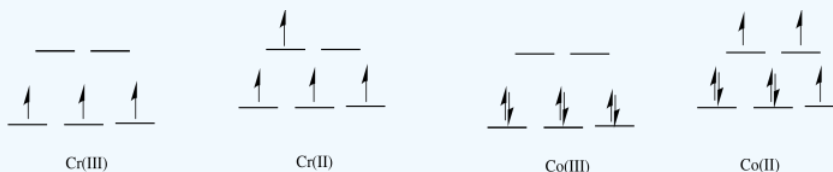
- octahedral

Answer b

- In the first row, 2^+ complexes are almost always high spin. However, 3^+ complexes are sometimes low spin.

Answer c

-



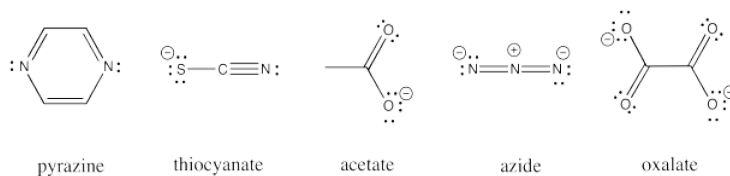
Answer d

- The Co(II) complex is high spin and labile. The ligands are easily replaced by water.

Answer e

- The Cr(III) complex is only d^3 ; it is inert.

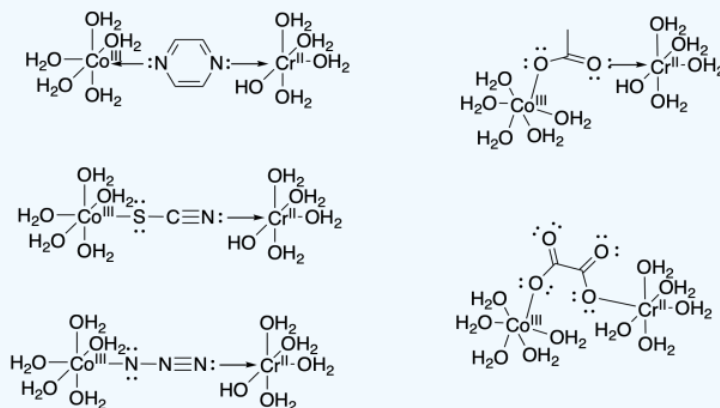
Other ligands can be involved in inner sphere electron transfers. These ligands include carboxylates, oxalate, azide, thiocyanate, and pyrazine ligands. All of these ligands have additional lone pairs with which to bind a second metal ion.



? Exercise 9.2.2.2

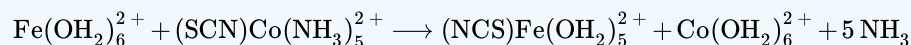
Draw an example of each of the ligands listed above bridging between a cobalt(III) and chromium(II) aqua complex.

Answer

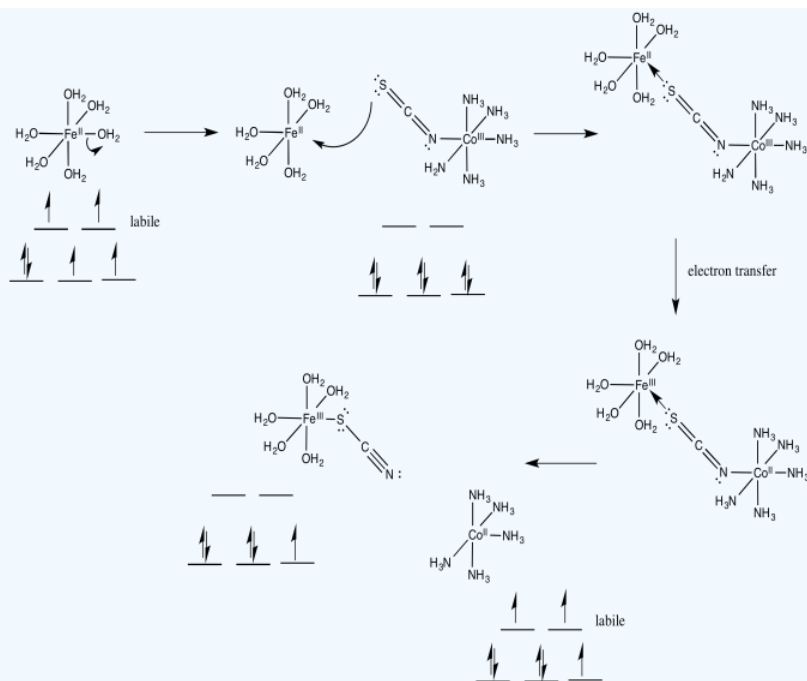


? Exercise 9.2.2.3

Explain, with structures and d orbital splitting diagrams, how the products are formed in the following reaction, in aqueous solution.



Answer



How does the electron travel over the bridge?

Once the bridge is in place, the electron transfer may take place via either of two mechanisms. Suppose the bridging ligand is a chloride. The first step might actually involve an electron transfer from chlorine to the metal; that is, the chloride could donate one electron from one of its idle lone pairs. This electron could subsequently be replaced by an electron transfer from metal to chlorine.



Sometimes, we talk about the place where an electron *used to be*, describing it as a "hole". In this mechanism, the electron donated from the bridging chloride ligand leaves behind a hole. The hole is then filled with an electron donated from the other metal.

Alternatively, an electron might first be transferred from metal to chlorine, which subsequently passes an electron along to the other metal. In the case of chlorine, this idea may be unsatisfactory, because chlorine already has a full octet. Nevertheless, some of the other bridging ligands may have low-lying unoccupied molecular orbitals that could be populated by this extra electron, temporarily.

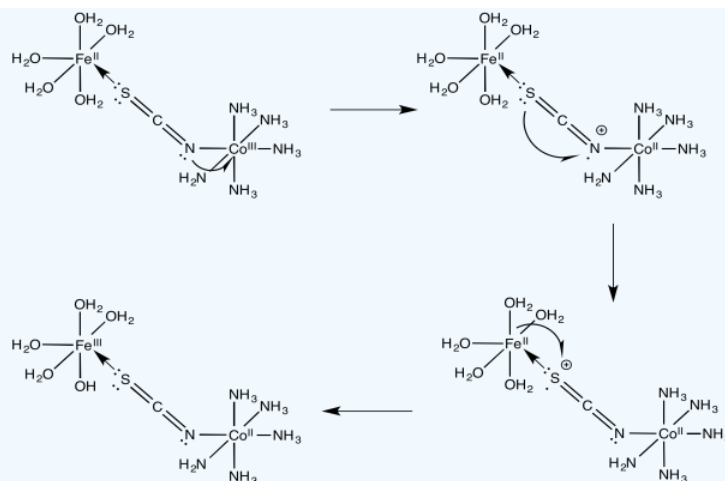


? Exercise 9.2.2.4

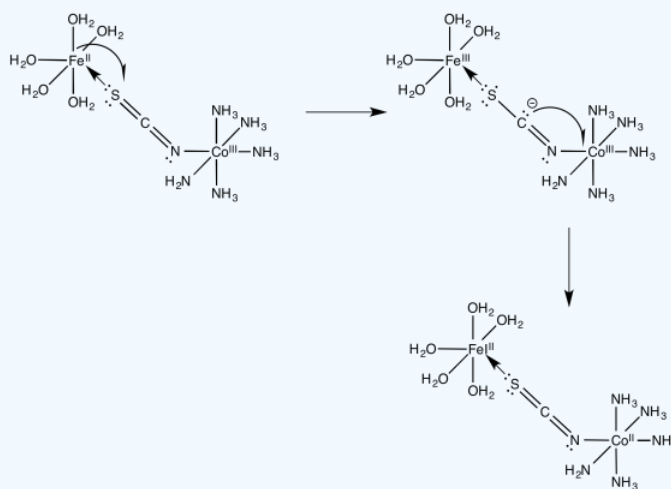
For the iron / cobalt electron transfer in problem Exercise 9.2.2.3(RO9.3.), show

- an electron transfer mechanism via a hole migration along the bridge
- an electron transfer mechanism via an electron migration along the bridge

Answer a



Answer b



? Exercise 9.2.2.5

One of the many contributions to the barrier for electron transfer between metal ions is internal electronic reorganization.

a) Draw d orbital splitting diagrams for each of the following metal ions in an octahedral environment.

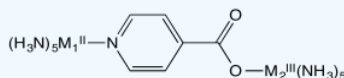
Ru(II) or Os(II)

Ru(III) or Os(III)

Co(II)

Co(III)

Flash photolysis is a method in which an electron can be moved instantly “uphill” from one metal to another (e.g. from M_2^{II} to M_1^{III} , below); the electron transfer rate can then be measured as the electron “drops” back from M_1^{II} to M_2^{III} .



b) Explain the relative rates of electron transfer reaction in this system, as measured by flash photolysis in the table below.

M_1^{II}	M_2^{III}	$k_{\text{obs}} \text{ s}^{-1}$
Os	Ru	$> 5 \times 10^9$

Os

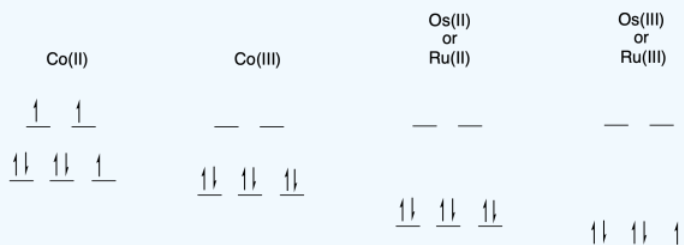
Co

1.9×10^5

c) Does the reaction above probably occur via an inner sphere or by an outer sphere pathway? Why?

Answer a

a)



Answer b

b) The electron transfer between Os(II) and Ru(III) will not involve any electron reorganization because both are low spin to begin with. However, the electron transfer between Os(II) and Co(III) will result in cobalt changing from low spin to high spin. The need to move electrons between different d orbitals on the cobalt will add to the barrier, slowing down the reaction.

Answer c

c) The pathway is probably inner sphere because of the bridging ligand. Furthermore, the conjugation in the bridging ligand would help in conducting an electron from one end of the ligand to the other, either through an electron mechanism or a hole mechanism.

? Exercise 9.2.2.6

Outer sphere electron transfer rates depend on the free energy change of the reaction (ΔG°) and the distance between oxidant and reductant (d) according to the relation

$$\text{Rate constant} = k = A e^{(-\Delta G)} e^{-d}$$

a) What happens to the rate of the reaction as distance increases between reactants?

One potential problem in measuring rates of intramolecular electron transfer (i.e. *within* a molecule) is competition from intermolecular electron transfer (*between* molecules).

b) What would you do in the flash photolysis experiment above to discourage intermolecular electron transfer?

c) How could you confirm whether you were successful in discouraging intermolecular reaction?

Answer a

a) The rate decreases exponentially as distance increases.

Answer b

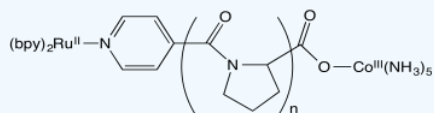
b) You might keep the concentration low in order to increase the distance between molecules, reducing the likelihood of an outer-sphere electron transfer.

Answer c

c) If you ran the experiment at a series of dilutions, intramolecular electron transfer would be unaffected but outer sphere electron transfer would not. If the rates were the same across a number of different concentrations, the reaction would probably be intramolecular.

? Exercise 9.2.2.7

Stephan Isied and coworkers at Rutgers measured the following electron transfer rates between metal centers separated by a peptide. (*Chem Rev* **1992**, 92, 381-394)



- The proline repeating unit is crucial in ensuring a steady increase in distance between metal centers with increased repeat units, n . Why?
- An inner sphere pathway in this case is expected to be somewhat slow because of the lack of conjugation in the polyproline bridge. Explain why.
- Plot the data below, with $\log k$ on the y axis (range from 4-9) and d on the x axis (12-24 Angstroms).

n	d (Å)	k_{obs} (s^{-1})
1	12.2	5×10^8
2	14.8	1.6×10^7
3	18.1	2.3×10^5
4	21.3	5.1×10^4
5	24.1	1.8×10^4

- d) A linear relationship is in agreement with Marcus theory; $\log k = -c \times d$. Is your plot linear?

Isied offers a number of possible explanations for the data, all of which involve two competing reaction pathways.

- e) Suggest one explanation for the data.

Answer a

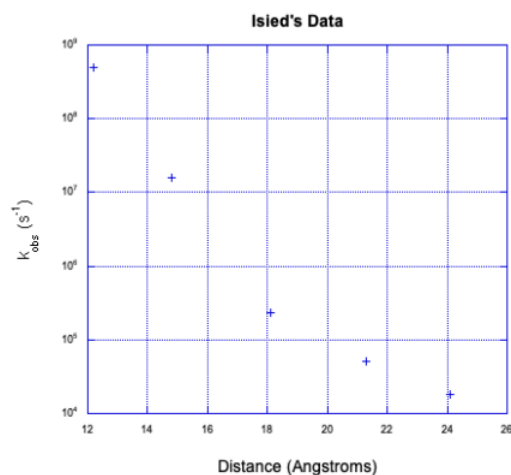
a) Rings are frequently used to introduce conformational rigidity (or decrease conformational flexibility), limiting the range of potential shapes a molecule could adopt. If the molecule can't wiggle around as much, then the distance between the ends of the molecule should be more constant.

Answer b

b) Although the ligand is bridging, it would be difficult to picture either an electron or hole mechanism of inner sphere electron transfer. There are few pi bonds or lone pairs to use as places to put electrons or temporarily remove electrons from, shuttling the electrons from place to place along the ligand. A conjugated system would be much more likely to carry out inner sphere electron transfer.

Answer c

c)



Answer d

d) The data is not linear.

Answer e

e) The data appear to show two lines that cross. That's a classic symptom of two competing mechanisms. The faster mechanism, to the left, is probably an intramolecular electron transfer. The slower mechanism, to the right, may be an intermolecular electron transfer.

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