

CHEM-457 PS6 Solutions

1.

MF&T #12.1

$[\text{Cr}(\text{H}_2\text{O})_6]^{2+}$ is labile, and has 4 unpaired electrons, with 1 in the anti-bonding e_g orbital. Occupation of this orbital renders substitution easier by leading to relatively weak chromium(II)–aqua ligand bonds. $[\text{Cr}(\text{CN})_6]^{4-}$ is inert. It has all 4 metal valence electrons in the bonding t_{2g} levels. These orbitals are rendered bonding in character due to π -backbonding with the cyanide ligands.

MF&T #12.3

Pentachlorooxochromate(V) is a d^1 complex; it should be labile, with vacancies in the t_{2g} levels.

Hexaiodomanganate(IV) is a d^3 complex; it should be inert.

Hexacyanoferrate(III) is a low-spin d^5 complex; it should be inert (vacant e_g levels).

Hexammineiron(III) is a d^6 high-spin complex; with partly occupied orbitals in both levels; it should be labile.

MF&T #12.5

$[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$ and $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ are high-spin species; the electrons in the upper e_g levels render them labile. $[\text{Cr}(\text{CN})_6]^{4-}$ is a d^4 low-spin species. The t_{2g} levels are unequally occupied and the e_g are vacant, which makes it a borderline complex in terms of substitution rate. $[\text{Cr}(\text{CN})_6]^{3-}$, $[\text{Fe}(\text{CN})_6]^{4-}$, and $[\text{Co}(\text{NH}_3)_5(\text{H}_2\text{O})]^{3+}$ are low-spin species with the t_{2g} levels either half filled or completely filled. This, combined with empty e_g levels, indicates inert species. LFAE approximations suggest that the activation energies for substitution reactions with these ions are relatively large.

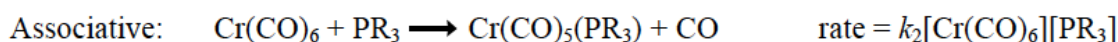
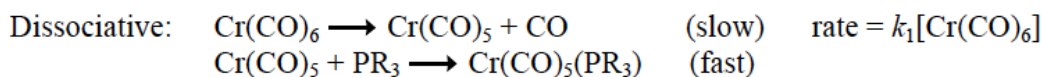
MF&T #12.8

- a. Because the rate is independent of the concentration of ^{13}CO , the rate determining step is most likely:



$\text{Cr}(^{12}\text{CO})_5$ then reacts rapidly with ^{13}CO .

- b. These terms describe two pathways to product, a dissociative pathway (as in part a) and an associative pathway:



With two mechanistic pathways leading to the same product, the overall rate is the sum of the rates of both.

- c. Bulky ligands will tend to favor the first order (dissociative pathway) because the crowding around the metal will favor dissociation and hinder association with incoming ligands. (This effect is discussed further in Section 14.1.1)

MF&T #12.13

a. $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = 10300 - 298 \times 55.6 = -6300 \text{ J/mol} = -6.3 \text{ kJ/mol}$

$$\Delta G^\circ = -RT \ln K; \ln K = -\Delta G^\circ/RT = 6300/(8.3145 \times 298.15) = 2.54; K = 12.7$$

- b. The *cis* isomer has the higher bond energy (actually, the lower overall energy and collectively stronger bonding), since rearrangement to the *trans* isomer is endothermic. Since the phosphines are better π acceptors, the *cis* isomer should be the more stable. If the phosphines are mutually *trans*, they compete for overlap with the same *d* orbitals, resulting in weaker bonds to Pt(II). When these phosphines are mutually *cis*, each can use one of the pair of d_{xz} and d_{yz} orbitals and avoid competition.
- c. The free phosphine must aid the isomerization via an associative mechanism. Since benzene is the solvent, and it is very nonpolar, it is not likely to assist the reaction. Only the second term of the rate equations of Problem 12.6 is significant here, with phosphine playing the role of the entering ligand.

MF&T #12.18

- a. The large negative entropy of activation implies that the activated complex is much more ordered than the reactants. This suggests an associative pathway.
- b. The iodo ligand leads to the fastest rate, involving bond breaking *trans* to the halogen, and therefore has the strongest *trans* effect.

MF&T #10.22

- a. NSe has the stronger *trans* effect. The longer Os—N₁ distance is consistent with weakening of this bond by the ligand *trans* to it, the NSe ligand.
- b. The short bond distance and large Os—N—Se angle (164.7°) suggest that the ligand has NSe⁺ character; the cation NSe⁺ would have a bond order of 3 and a very short bond-distance. It is also worth noting that the N—Se stretching vibration in this complex is much higher (by 211 cm⁻¹) than in gas phase NSe.

MF&T #13.12

Sulfur is less electronegative than oxygen. Therefore, the tungsten in $W(S)Cl_2(CO)(PMePh_2)_2$ has greater electron density and a greater tendency to participate in π -backbonding with CO; a lower energy $\nu(CO)$ is expected (actual value: 1986 cm^{-1}).

MF&T #10.13

Adding electrons to a carbonyl complex puts more electrons into the back-bonding t_{2g} orbitals. As a result, the V–C bonds in $[V(CO)_6]^-$ are strengthened and the distance shortened (but the C–O bonds are weakened by having more electrons in the t_{2g} orbitals, that are antibonding with respect to the C–O bonds.).

MF&T #13.15

- a. If NO is counted as a linear donor, each of these has 18 electrons. The increasing nuclear charge (from formally Cr(0) to Mn(I) to Fe(II)) results in progressively less backbonding to the ligands and an increase in N–O bond order, leading to the higher NO stretching frequencies. The Cr species has an exceptionally low NO stretching frequency. It may have bent NO coordination, rendering it a 16 electron ion formally containing Cr(II). The Fe complex has a rather high NO stretching frequency, suggesting that π -backbonding is not a very large contribution to the electronic ground state of this complex.
- b. The low energy band indicates bent NO coordination; the higher energy band is from the linear ligand. This complex has one of each, with angles of 138° and 178° (Greenwood and Earnshaw, *Chemistry of the Elements*, 2nd ed., pp. 450-52).

2. The structure on the right has a total electron count of 18-electrons, while that on the left has an electron count of 16-electrons. The 18-electron configuration is more stable and hence, the structure on the right will be favored.
3. We did not get to cover insertion chemistry – you are not responsible for the material needed to solve this problem.