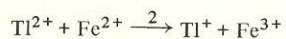


PROBLEMS

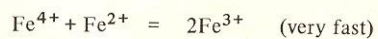
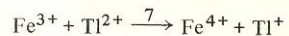
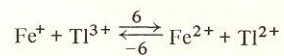
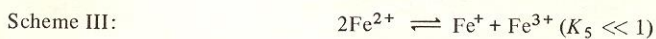
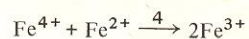
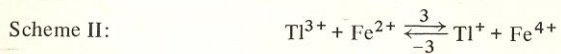
5-1 *Multistep reactions; limiting forms; equivalent mechanisms.* Consider scheme I for the net reaction $2\text{Fe}^{2+} + \text{Tl}^{3+} = 2\text{Fe}^{3+} + \text{Tl}^{+}$:



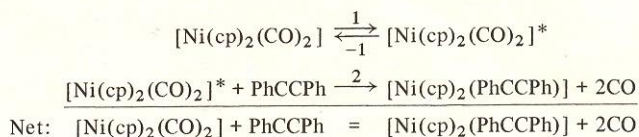
(a) Derive the rate expression making the steady-state approximation for $[\text{Tl}^{2+}]$.

(b) To what simpler forms does this reduce under what limiting conditions?

(c) Are, and under what conditions, schemes II and III distinguishable from I?



5-2 *Rate law and mechanism.* Cetini et al. [*Inorg. Chem.*, 10:2672 (1971)] propose this mechanism:



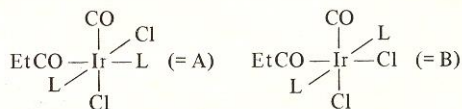
in which $[\text{Ni}(\text{cp})_2(\text{CO})_2]^*$ represents a steady-state intermediate of rearranged structure.

(a) Derive the differential rate expression. Designate the pseudo-first-order rate constant k_{obs} . Prove that $1/k_{\text{obs}}$ versus $1/[\text{PhCCPh}]$ should be linear (i.e., $1/k_{\text{obs}} = \text{intercept} + \text{slope}/[\text{PhCCPh}]$).

(b) Assuming each of the three individual rate constants follows the Arrhenius equation, $k_i = A_i \exp(-E_i/RT)$, identify the exact quantity given by the slope of the following plots:

1. $\ln(1/\text{intercept})$ versus $1/T$
2. $\ln(\text{slope}/\text{intercept})$ versus $1/T$

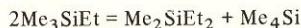
5-3 *Rate law and mechanism.* Write a mechanism consistent with the following observations, and give the algebraic relation between the constants of your mechanism and those in the experimental rate law. Mawby and coworkers [*J. Chem. Soc. Dalton*, 220 (1973)] report that the isomerization of A to B



follows the rate expression (L is a phosphine, PMe_2Ph).

$$\frac{d[\text{B}]}{dt} = \frac{P[\text{A}]}{1 + Q[\text{L}]}$$

5-4 *Rate law and mechanism.* The redistribution of alkyl groups on silanes as in the equation

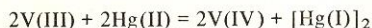


is catalyzed in benzene solution by aluminum bromide according to the rate expression

$$\frac{-d[\text{Me}_3\text{SiEt}]}{dt} = \frac{\alpha[\text{Me}_3\text{SiEt}]^2[\text{Al}_2\text{Br}_6]}{1 + \beta[\text{Me}_3\text{SiEt}]}$$

Propose a mechanism to account for this result and show how the rate constants for the elementary reactions are related to α and β .

5-5 *Rate law and mechanism.* The net reaction



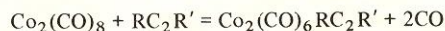
has a rate term showing the following concentration dependences

$$\frac{-d[\text{V(III)}]}{dt} = \frac{A[\text{V(III)}]^2[\text{Hg(II)}]}{B[\text{V(IV)}] + [\text{V(III)}]}$$

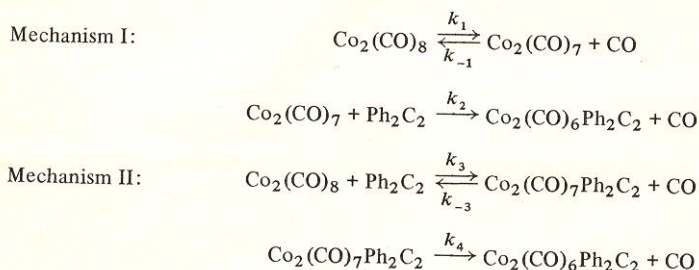
Suggest a mechanism consistent with this rate expression noting that on the time scale of this reaction the following are fast and lie far to the right



5-6 *Rate law and mechanism.* P. C. Ellgen [*Inorg. Chem.*, 11:691 (1972)] has studied the reaction of dicobalt octacarbonyl with alkynes:

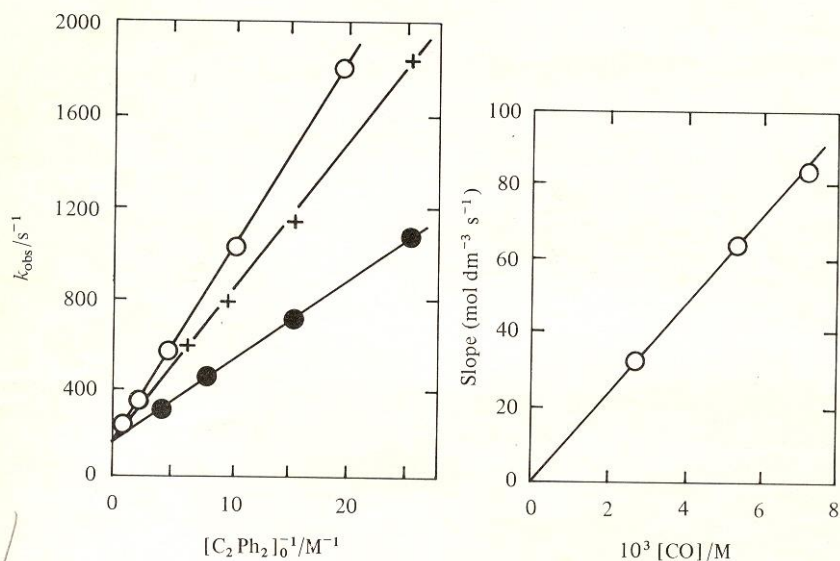


under conditions in which $[RC_2R']$ and $[CO]$ were in large excess over $[Co_2(CO)_8]$. The symbol k_{obs} represents the pseudo-first-order rate constant defined by the relation $-d \ln [Co_2(CO)_8]/dt$. Consider the following two mechanisms:



(a) For each mechanism derive an expression for k_{obs} . Make the steady-state assumption for the intermediate.

(b) What (be specific) do the following observations reveal about the correctness of either mechanism? k_{obs} is a linear function of $1/[C_2Ph_2]_0$ at constant $[CO]$, and the slope of the plot varies directly with $[CO]$. Provide numerical values for any rate constants or rate constant combination you can on the basis of these data.



5-7 Reaction mechanism. The reaction of dichromate ion with dihydrogen, $Cr_2O_7^{2-} + 3H_2 + 8H^+ = 2Cr^{3+} + 7H_2O$, is very slow, but it is catalyzed by salts of Cu^{2+} and Ag^+ according to the following rate laws [J. Halpern et al., *J. Phys. Chem.*, 60:1455 (1956); 61:1239 (1957)]:

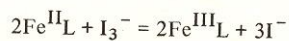
Cu^{2+} catalysis:
$$\frac{-d[Cr_2O_7^{2-}]}{dt} = \frac{k_{Cu}[Cu^{2+}]^2[H_2]}{[Cu^{2+}][H^+]}$$

Ag^+ catalysis:
$$\frac{-d[Cr_2O_7^{2-}]}{dt} = k_{1Ag}[Ag^+]^2[H_2] + k_{2Ag}[Ag^+][H_2]$$

Interpret (separately) these observations in terms of reaction mechanisms.

$[H^+]$	$10^3 [(CO_2H)_2]$	A	B
0.030	0.50	5.88	1.12
0.030	10.00	118	1.24
0.100	2.00	25.0	4.0
0.100	3.00	38.8	3.75
0.100	15.00	192	4.30
0.300	2.00	25.3	11.7
0.300	5.00	58.8	11.3
0.600	5.00	66.7	21.8

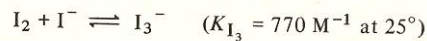
5-10 Preequilibria and reaction mechanism. Woodruff, Weatherburn, and Margerum [*Inorg. Chem.*, 10:2102 (1971)] have studied the oxidation of certain Fe(II) complexes (Fe^{II}L) by iodine-triiodide solutions.



The rate is first-order in $[Fe^{II}L]$ and first-order in total iodine concentration $[I_2]_T$ (where $[I_2]_T = [I_2] + [I_3^-]$):

$$\frac{-d[I_2]_T}{dt} = k_0 [Fe^{II}L] [I_2]_T$$

A correction was applied for the equilibrium



Prove that the data shown are consistent with parallel rate-limiting reactions of I_2 and I_3^- and evaluate k_1 and k_2 at 25.0° .

