CHAPTER

FIVE

DEDUCTION OF REACTION MECHANISMS

The route leading from kinetic data to reaction mechanism is not always a straightforward one. The first step is to convert the experimental data, which most often take the form of concentration as a function of time, to a differential rate expression, which gives reaction rate as a function of concentration(s). The first four chapters of this book have been concerned with that aspect of the problem. The next consideration is the interpretation of the rate law to reveal the family of chemical reactions which comprise the mechanism.

Once one mechanism which is consistent with the data at hand is found, two further considerations immediately arise. First, what other mechanisms will also fit the existing data? Second, are there additional experiments, kinetic determinations or otherwise, which permit some of the possibilities to be ruled out?

5-1 THE ACTIVATED COMPLEX OR TRANSITION STATE

Every elementary reaction proceeds through a critical complex corresponding to the state of potential-energy maximum along its reaction coordinate. In kinetics we are primarily concerned with the highest energy step (or steps) along the entire potential-energy surface, which corresponds to the critical activation process. To a lesser extent we may also consider any rapid reactions which precede or follow the rate-limiting step(s).

One goal of both theory and experimental kinetics is a full understanding of the activation process—the evolution of structure and energetics accompanying the molecular transformations in the reactants as they proceed along the reaction coordinate toward the activated complex. This level of understanding has as yet been attained only in some quite simple elementary reactions.

For most "real" systems we settle for far less, and we will seek the answers to questions such as the number of transition states, whether they occur sequentially or in parallel, and whether chemical reaction intermediates are involved. Kinetic data and related experiments will answer those questions, particularly those relating to the composition of the activated complex.

We need to distinguish between an *intermediate* and an *activated complex*. The former lies at a potential-energy minimum along the reaction coordinate: Further activation, which might be intramolecular distortion or rearrangement, or subsequent bimolecular reaction with a different chemical component, is needed to convert the intermediate to the activated complex leading to products. The activated complex is necessarily decomposing into products of reaction (or to substances which themselves lead to the products); that is the only type of reaction it can undergo. The intermediate was itself preceded by another activated complex; both activated complexes lie at potential-energy maxima.

An intermediate might coincidentally have the same composition as an activated complex, but it is not identical with it. The intermediate has a choice of reactions; among the reactions are reconversion to starting material and reaction with a trapping reagent. It might have nearly the same geometry as the activated complex as well, but some distortion or other activation process would be needed before the intermediate could become an activated complex.

The concentrations appearing in the rate expression provide directly the "composition" (the elements which are present and the ionic charge, if any) of each activated complex for every elementary reaction in the mechanistic array that can be a rate-limiting step under the conditions studied. It therefore gives the number of separate activation steps needed, and it provides an indication of whether they occur in parallel or sequentially.

5-2 MECHANISTIC INTERPRETATION OF RATE LAWS

Certain features of mechanism manifest themselves in a regular way, and they serve as guides in formulating one or more mechanisms consistent with the data. Listed here is this set of "rules," more properly to be regarded as "clues," useful in formulating the mechanism. Later sections in this chapter amplify certain points.

1. *The concentration dependences in the rate law establish the elemental composition and charge of the activated complex(es).*

The rate law for the reaction of ClO_2^- and I^- in acidic solution is

$$\frac{-d[ClO_2^-]}{dt} = k[ClO_2^-][I^-][H^+] \tag{5-1}$$

This rate law is consistent with a single activated complex of composition $[HClO_2I^- \pm n(H_2O)]^{\ddagger}$. The involvement of solvent water cannot be defined, since its concentration

is not varied. A second example is the oxidation of oxalic acid by chlorine,

$$Cl_2 + (COOH)_2 = 2CO_2 + 2Cl^- + 2H^+$$

which follows the rate law

$$\frac{d[CO_2]}{dt} = \frac{k[Cl_2][(COOH)_2]}{[H^+]^2[Cl^-]} \tag{5-2}$$

The composition of the activated complex is thus $[Cl_2 + (COOH)_2 - 2H^+ - Cl^- \pm nH_2O]^\ddagger$, or $[C_2O_4Cl(H_2O)_n^-]^\ddagger$. If the rate law consists of more than a single term, either numerator or denominator terms, the mechanism consists of as many activated complexes as there are terms in the rate law. The composition of each is given by the same procedures as shown here, letting each term predominate in turn. Examples are given under rules 3 and 4.

2. *A rate law to be properly interpreted according to rule 1 above must be written in terms of the predominant species in the reaction medium.*

That is to say, we must take due account of pertinent equilibria and use the equilibrium relations to convert the experimental rate law, which will often be expressed in terms of stoichiometric concentrations, to a form containing only the concentrations of the predominant species. This point will be amplified in Sec. 5-6, and we need note here only one trivial example. The rate law of Eq. (5-1) contains the product of concentrations, $[H^+][I^-]$. Were the experiments carried out by using HI as the source of H^+ and I^- ions, the rate would be proportional to the square of the laboratory concentration, C_{HI}^2. That relation holds because HI is a strong electrolyte in water, so that $[H^+] = [I^-] = C_{HI}$. Yet were the observation taken literally, without recognition of the dissociation of HI, application of rule 1 would suggest that the activated complex contains two molecules of HI rather than the elements of one HI molecule.

3. *The number of (positive) numerator terms in a rate law is the number of parallel pathways involving transition states of different composition.*

By way of example, the reaction $3I^- + H_2O_2 + 2H^+ = I_3^- + 2H_2O$ proceeds according to a rate law having two (numerator) terms:

$$\frac{d[I_3^-]}{dt} = k[H_2O_2][I^-] + k'[H_2O_2][H^+][I^-] \tag{5-3}$$

indicating two parallel pathways with transition states of composition $[H_2O_2I^-]^\ddagger$ and $[H_3O_2I]^\ddagger$.

A negative numerator term results from a reverse reaction, one term for each pathway, reflecting the approach to equilibrium. The classic S_N2 mechanism for

$$RX + Y^- \underset{k_r}{\overset{k_f}{\rightleftharpoons}} RY + X^-$$

has a rate law

$$\frac{-d[RX]}{dt} = k_f[Y^-][RX] - k_r[RY][X^-]$$

If the mechanism is expressed as the rate constant for the approach to equilibrium, a summation of two terms is found, which, when X^- and Y^- are present in large excess, takes the form $k_{obs} = k_f[X^-] + k_r[Y^-]$. But one is careful to note that this corresponds to one activated complex, not two. That is, the summation of terms arises in this case because the expression for k_{obs} is not the expression for the reaction rate itself.

4. *A summation of terms in the denominator indicates a mechanism consisting of successive steps; one or more of the steps is a reversible reaction.*

The number of denominator terms indicates the number of sequential activated complexes. That is, it gives the number of reaction steps, excluding, of course, any rapid reactions occurring before or after. The denominator terms represent the competitive reactions of an intermediate, and the inequalities of the rate constant-concentration composites which lead to a given limiting form are equivalent to a change in rate-limiting step from one of the reaction steps to the other. The composition of each transition state in the succession of reaction steps is inferred according to rule 1.

The reaction $2Fe^{2+} + Tl^{3+} = 2Fe^{3+} + Tl^+$ constitutes an instructive example. It follows the rate law

$$\frac{-d[Tl^{3+}]}{dt} = \frac{k[Fe^{2+}]^2[Tl^{3+}]}{[Fe^{2+}] + k'[Fe^{3+}]} \tag{5-4}$$

This requires two activated complexes whose compositions are obtained by considering first one denominator term and then the other to predominate. The limiting rate equation when $[Fe^{2+}] \gg k'[Fe^{3+}]$ is $-d[Tl^{3+}]/dt = k[Fe^{2+}][Tl^{3+}]$, with activated complex $[TlFe^{5+}]^{\ddagger}$. With the reverse inequality, the rate is proportional to $[Fe^{2+}]^2[Tl^{3+}]/[Fe^{3+}]$, which corresponds to the activated complex $[TlFe^{4+}]^{\ddagger}$. A mechanism consistent with that is the following, where Tl^{2+} is an intermediate for which the steady-state approximation is valid:

$$Fe^{2+} + Tl^{3+} \rightleftharpoons Fe^{3+} + Tl^{2+} \tag{5-5}$$

$$Fe^{2+} + Tl^{2+} \longrightarrow Fe^{3+} + Tl^+ \tag{5-6}$$

5. *Concentrations appearing in single-term denominators are the chemical products of step(s) prior to the rate-limiting step.*

This is a special case of rule 4. The rate law for chlorine and oxalic acid, Eq. (5-2), suggests that two H^+ ions and one Cl^- ion are produced in equilibria established rapidly (compared to the overall rate). Such equilibria *may be* (see Sec. 5-3) the following:

$$Cl_2 + H_2O \rightleftharpoons HOCl + Cl^- + H^+ \tag{5-7}$$

$$H_2C_2O_4 \rightleftharpoons H^+ + HC_2O_4^- \tag{5-8}$$

Needless to say, we do not learn any details about the *mechanisms* of such rapid equilibria.

6. *The sum of the mechanistic steps must be the overall chemical reaction; rapid reactions may follow the rate-limiting step(s).*

Thus the reaction $2Cr^{2+} + Tl^{3+} = 2Cr^{3+} + Tl^+$ occurs by the rate law

$$\frac{-d[Tl^{3+}]}{dt} = k[Cr^{2+}][Tl^{3+}] \tag{5-9}$$

consistent with either of these mechanisms:

Mechanism I:	$Cr^{2+} + Tl^{3+} \longrightarrow Cr^{3+} + Tl^{2+}$	slow	(5-10)
	$Cr^{2+} + Tl^{2+} \longrightarrow Cr^{3+} + Tl^+$	rapid	(5-11)
Mechanism II:	$Cr^{2+} + Tl^{3+} \longrightarrow Cr^{4+} + Tl^+$	slow	(5-12)
	$Cr^{2+} + Cr^{4+} \longrightarrow 2Cr^{3+}$	rapid	(5-13)

where the alternative rapid reactions are added for sake of consistency with the overall stoichiometry of the reaction. The following points deserve note: (*a*) the information in Eq. (5-9) does not distinguish between the alternatives; (*b*) this kinetic study provides no information concerning the mechanism of either postulated rapid reaction, (5-11) or (5-13); (*c*) the lower power for $[Cr^{2+}]$ in the kinetic equation compared to the stoichiometric reaction (1 versus 2) indicates that a reaction intermediate is produced and then consumed in a subsequent rapid step.

7. *Alternative mechanisms leading to the same pattern of activated complexes are not kinetically distinguishable.*

Since both steps 10 and 12 have an activated complex $[CrTl^{5+}]^{\ddagger}$, the rate law of Eq. (5-9) cannot afford a choice between them. Among the further options we might consider are these two: (*a*) a wider range of concentration variation, particularly experiments with added Cr^{3+}, added Tl^+, and/or a lower concentration of Cr^{2+}, may elicit additional kinetic terms and transform Eq. (5-9) to a form analogous to the more informative Eq. (5-4). (*b*) A comparison of the chemistry of the proposed intermediates Tl^{2+} and Cr^{4+} to suggest which is the more reasonable formulation. The evidence may be thermodynamic (dealing with the stability of such intermediates), stereochemical, structural, or chemical or it may be based upon the reaction products formed. Here the experimenter has the chance to bring skill and ingenuity to bear on the problem of providing critical tests of mechanism. In the present instance the Cr(III) product proved to be $[(H_2O)_4Cr(OH)_2Cr(OH_2)_4]^{4+}$ rather than $Cr(H_2O)_6^{3+}$, which is suggestive of mechanism II.

8. *An increase of reaction order with increasing concentration suggests parallel pathways, whereas a decrease in order suggests a sequence of steps.*

This is an alternative expression of statements 3 and 4. Note the order with respect to $[H^+]$ increases with $[H^+]$ in Eq. (5-3), whereas the orders in $[Fe^{2+}]$ and $[Fe^{3+}]$ in reaction (5-4) decrease with an increase in the concentration of the ion in question.

5-3 EQUIVALENT KINETIC EXPRESSIONS

As stated earlier, the rate of reaction of oxalic acid and chlorine,

$$Cl_2 + H_2C_2O_4 = 2CO_2 + 2Cl^- + 2H^+ \tag{5-14}$$

when expressed in terms of the predominant species in solutions, is given by[1]

$$\frac{-d[Cl_2]}{dt} = k\,\frac{[Cl_2][(COOH)_2]}{[H^+]^2[Cl^-]} \tag{5-15}$$

The following are rapidly established equilibria:

$$Cl_2 + H_2O \overset{K_d}{\rightleftharpoons} HOCl + Cl^- + H^+ \tag{5-16}$$

$$HOCl \overset{K_a}{\rightleftharpoons} H^+ + OCl^- \tag{5-17}$$

$$H_2C_2O_4 \overset{K_1}{\rightleftharpoons} H^+ + HC_2O_4^- \tag{5-18}$$

$$HC_2O_4^- \overset{K_2}{\rightleftharpoons} H^+ + C_2O_4^{2-} \tag{5-19}$$

By appropriate substitution, it can be readily shown that the following expressions are equivalent to the original rate expression

$$k_1\,\frac{[Cl_2][HC_2O_4^-]}{[H^+][Cl^-]} \qquad k_2\,\frac{[Cl_2][C_2O_4^{2-}]}{[Cl^-]}$$

$$k_3[HOCl][HC_2O_4^-] \qquad k_4[OCl^-][H_2C_2O_4] \tag{5-20}$$

It is pointless to argue whether the kinetic data support a rate-limiting step consisting of the bimolecular reaction of HOCl with $HC_2O_4^-$ or of OCl^- with $H_2C_2O_4$. The rate law prescribes *only* the composition of the activated complex—and neither the order in which the components come together nor the mode by which they are bonded. Perhaps "chemical" arguments or comparison reactions† can make a case for one formulation or the other, but the bare kinetic equations do not.

It might be commented that Eq. (5-15) remains the best form in which to express the data obtained in acidic solution, because the rate is expressed in terms of the species predominating under those circumstances. If one then wishes to interpret the data in terms of a specific bimolecular process, say the reaction of $HC_2O_4^-$ with HOCl,

†For example: Does the dimethyl ester of oxalic acid react with OCl^-? Does the monomethyl ester react with HOCl?

then a derived rate constant [k_3 of Eq. (5-20)] can be calculated from the relation

$$k_3 = \frac{k}{K_d K_1} \tag{5-21}$$

This point is especially well kept in mind if the equilibrium constants are known only very poorly, as may be the case for very feeble associations, or if a long extrapolation of experimental conditions is required. In such cases, one should always report the rate constant values resulting directly from the experimental conditions. For purposes of discussion or comparison, one might later wish to convert the precise experimental value into an approximate derived value, recognizing all the while that the latter constitutes an interpretation of the investigator. In so doing it is assumed first that the choice of elementary mechanistic steps is correct and secondly that the necessary equilibrium constant(s) can be estimated with sufficient precision for the comparison purposes at hand.

By way of example, Hicks and Sutter[2] found that the reaction of permanganate ion with tris-(1,10-phenanthroline)iron(II) ion contained a kinetic term of the form

$$\frac{-d[MnO_4^-]}{dt} = (k_1 + k_2[H^+])[MnO_4^-][Fe(phen)_3^{2+}] \tag{5-22}$$

and gave these values: $k_1 = (6.1 \pm 2.2) \times 10^3\ M^{-1}\ s^{-1}$, $k_2 = (7.42 \pm 0.11) \times 10^5\ M^{-2}\ s^{-1}$. If the second term is *interpreted* as being the bimolecular reaction of permanganic acid with $Fe(phen)_3^{2+}$,

$$HMnO_4 + Fe(phen)_3^{2+} \xrightarrow{k_2'} HMnO_4^- + Fe(phen)_3^{2+}$$

then the bimolecular rate constant k_2' can be calculated from the experimental k_2 and K_a for permanganic acid.

$$HMnO_4 \overset{K_a}{\rightleftharpoons} H^+ + MnO_4^- \tag{5-23}$$

The value for K_a is $\sim 3 \times 10^2$ M, which gives $k_2' = k_2 K_a = \sim 2 \times 10^8\ M^{-1}\ s^{-1}$. Clearly this value of K_a is *highly* approximate, considering the practical difficulties attending the evaluation of the ionization constant of such a strong acid. The approximate k_2' may nonetheless be useful in that it can be directly compared with k_1; for example, one might note that $HMnO_4$ is some $10^{4.7}$ times more reactive than MnO_4^- toward $Fe(phen)_3^{2+}$. The value of the direct experimental value of k_2 is, however, likely to be of more lasting significance than the derived and approximate k_2'. Workers finding a situation such as that should be certain to report the former, whether or not they choose to estimate the latter for comparison purposes. It is also to be noted that the assignment of Eq. (5-23) as the mechanism for this pathway is only one of the possible interpretations; protonation of the other reactant followed by the bimolecular reaction of MnO_4^- and $Fe(phen)_2(phenH)^{3+}$ is a realistic alternative.

Another example is afforded by the reaction of iodide and hypochlorite ions,

$$I^- + OCl^- = OI^- + Cl^- \tag{5-24}$$

in 0.1 to 1.0 M potassium hydroxide. The rate expression is

$$\frac{d[OI^-]}{dt} = \frac{k[I^-][OCl^-]}{[OH^-]} \tag{5-25}$$

Given the uncertainty in the order with respect to solvent, the composition of the activated complex is $[H_2O + I^- + OCl^- - OH^-]^{\ddagger}$. This suggests the following mechanism:

$$OCl^- + H_2O \rightleftharpoons HOCl + OH^- \quad \text{rapid} \tag{5-26}$$

$$I^- + HOCl \longrightarrow HOI + Cl^- \quad \text{slow} \tag{5-27}$$

$$OH^- + HOI = H_2O + IO^- \quad \text{rapid} \tag{5-28}$$

$$I^- + OCl^- = OI^- + Cl^- \quad \text{overall} \tag{5-29}$$

Thus

$$\frac{d[IO^-]}{dt} = k_{27}[I^-][HOCl] \tag{5-30}$$

$$\frac{d[IO^-]}{dt} = \frac{k_{27}K_{26}[I^-][OCl^-]}{[OH^-]} \tag{5-31}$$

Because the experiments were done in strongly basic solution, Eq. (5-25) is a better representation of the actual results than (5-30). The latter may be useful for other purposes, however, particularly for the discussion of mechanism. The elementary rate constant k_{27} may be calculated by the relation $k_{27} = k/K_{26}$, provided K_{26} has a known value.

The maximum rate of a bimolecular reaction is limited in solution by the diffusion and in the gas phase by the collision frequency of the two solutes. The theoretical considerations are given later, Secs. 9-2 and 8-1, but it is helpful to consider the implications of those results in the present discussion of mechanistic alternatives. The maximum rate constant for a bimolecular step is ca. 10^{10} dm^3 mol^{-1} s^{-1} in water at 298 K. (The value differs little with solvent and temperature, but it may be modified somewhat if the reactants are ions.) Suppose that a mechanism under consideration contains a bimolecular step having a rate constant considerably in excess of that value. The mechanism, or at least this step, can consequently be ruled out. In effect, this prohibits mechanisms requiring the reaction of a species accessible only by quite unfavorable equilibria. An illustration is helpful. The reaction of $Cr^{2+}(aq)$ and $Co(NH_3)_5H_2O^{3+}$ according to the equation

$$Cr^{2+}(aq) + Co(NH_3)_5H_2O^{3+} + 5H^+ = Cr^{3+} + Co^{2+} + H_2O + 5NH_4^+$$

follows the rate law

$$\frac{-d[Cr^{2+}]}{dt} = \frac{k[Cr^{2+}][Co(NH_3)_5H_2O^{3+}]}{[H^+]}$$

with k = 3.1 dm^3 mol^{-1} s^{-1}. Two ready interpretations come to mind: One metal complex undergoes hydrolysis,

$$Cr^{2+} + H_2O = CrOH^+ + H^+ \quad (\text{rapid}, K_{a,Cr} \approx 10^{-11} \text{ mol dm}^{-3})$$

$$Co(NH_3)_5H_2O^{3+} + H_2O = Co(NH_3)_5OH^{2+} + H_3O^+$$

$$(\text{rapid}, K_{a,Co} = 2.5 \times 10^{-7} \text{ mol dm}^{-3})$$

and the hydrolyzed form reacts with the other metal ion complex. The alternative rate-limiting steps are then

$$CrOH^+ + Co(NH_3)_5H_2O^{3+} \xrightarrow{k_1} CrOH^{2+} + Co(NH_3)_5H_2O^{2+}$$

$$Cr^{2+} + Co(NH_3)_5OH^{2+} \xrightarrow{k_2} Cr^{3+} + Co(NH_3)_5OH^+$$

In both cases these processes would be followed by further rapid steps which are easily written down. The values of the rate constants for the elementary reactions are then $k_1 = k/K_{a,Cr} \approx 3 \times 10^{11}$ dm^3 mol^{-1} s^{-1} and $k_2 = k/K_{a,Co} = 1.2 \times 10^7$ dm^3 mol^{-1} s^{-1}. The former can be ruled out on the basis that the value of k_1 exceeds by a factor of about 30 the maximum limit allowed; in fact, the discrepancy is undoubtedly greater than that considering the ionic charges have the same signs.

5-4 PARALLEL PATHWAYS

Consider the reaction

$$3I^- + H_2O_2 + 2H^+ = I_3^- + 2H_2O \tag{5-32}$$

which proceeds according to the rate law

$$\frac{d[I_3^-]}{dt} = k_2[H_2O_2][I^-] + k_3[H_2O_2][H^+][I^-] \tag{5-33}$$

Clearly, the reaction occurs by two independent pathways, the first of which might correspond to rate-determining S_N2 displacement of OH^- by I^-:

$$H_2O_2 + I^- \longrightarrow HOI + OH^- \quad \text{slow} \tag{5-34}$$

$$H^+ + OH^- \rightleftharpoons H_2O \quad \text{very rapid} \tag{5-35}$$

$$HOI + H^+ + 2I^- = I_3^- + H_2O \quad \text{rapid} \tag{5-36}$$

The sum of the reactions corresponds to the net Eq. (5-32), and the slow step results in the proper composition for the activated complex. The rapid steps following the rate-determining step are speculative and are added primarily for completeness rather than mechanistic detail. It is only for that reason that Eq. (5-36) contains four reactants; in no way does it suggest a four-body collision. On the contrary, no mechanistic information or detail about the fast steps is obtained from this work.

The second path can be described by either of the schemes (5-37) and (5-38) or (5-39) and (5-40) followed in each case by fast reaction such as (5-36).

$$H^+ + I^- \rightleftharpoons HI \qquad \text{rapid} \qquad (5\text{-}37)$$

$$HI + H_2O_2 \longrightarrow H_2O + HOI \qquad \text{slow} \qquad (5\text{-}38)$$

$$H_2O_2 + H^+ \rightleftharpoons H_2OOH^+ \qquad \text{rapid} \qquad (5\text{-}39)$$

$$H_2OOH^+ + I^- \longrightarrow H_2O + HOI \qquad \text{slow} \qquad (5\text{-}40)$$

In any case, the second term in the rate law gives the composition of the activated complex as $[H_2O_2HI]^+$. The mechanistic details are somewhat less definitive; on chemical grounds one might prefer (5-39) and (5-40) over (5-37) and (5-38) (since the oxygen atom of H_2O_2 is more basic than an I^- ion and since a ready interpretation of 40 as the S_N2 displacement of H_2O by the nucleophile I^- is at hand), but such interpretation clearly goes beyond the immediate kinetic data.

5-5 SUCCESSIVE STEPS

Consider first a two-step sequence involving a single intermediate. For the net reaction

$$A + 2B = C + 2D \qquad (5\text{-}41)$$

proceeding according to this mechanism

$$A + B \underset{2}{\overset{1}{\rightleftharpoons}} X + D \qquad (5\text{-}42)$$

$$X + B \underset{4}{\overset{3}{\rightleftharpoons}} C + D \qquad (5\text{-}43)$$

the steady-state rate law can be derived by first solving for $[X]_{ss}$ and then expressing $-d[A]/dt$ in terms of concentrations of major species. Thus

$$[X]_{ss} = \frac{k_1[A][B] + k_4[C][D]}{k_2[D] + k_3[B]} \qquad (5\text{-}44)$$

$$\frac{-d[A]}{dt} = k_1[A][B] - k_2[X][D] \qquad (5\text{-}45)$$

$$\frac{-d[A]}{dt} = \frac{k_1k_3[A][B]^2 - k_2k_4[C][D]^2}{k_3[B] + k_2[D]} \qquad (5\text{-}46)$$

The negative numerator term in Eq. (5-46) arises from the reverse reaction. It is instructive to examine the form the rate law takes if the reaction is effectively irreversible. It will be if equilibrium lies far to the right, either because the equilibrium constant K $(= k_1k_3/k_2k_4)$ is very large or because forcing concentrations of reactants are used. The requisite condition for neglecting the back reaction is $[C][D]^2/[A][B]^2 \ll K$. In that event the rate law simplifies to

$$\frac{-d[A]}{dt} = \frac{k_1k_3[A][B]^2}{k_2[D] + k_3[B]} \qquad (5\text{-}47)$$

which is equivalent to having set $k_4 = 0$ in the derivation. Note that, according to Eq. (5-47), the concentration of a product D may lower the rate of a reaction even though the reverse reaction is unimportant. This is an important point: retardation by a product does not *necessarily* mean that one is approaching equilibrium. Another very common effect of a product, as shown here, is to lower the reaction rate by diverting the intermediate back to product. The term $k_2[X][D]$ in the present example represents this contribution.

In this example the order with respect to [B] decreases from 2 to 1 with increasing [B] and the order with respect to [D] also decreases from 0 to −1 with increasing [D]. The decrease in order with increase in concentration is the sign of a stepwise mechanism, the number of steps being the number of denominator terms.

The summation of denominator terms indicates competition for an intermediate. The rate law is not uniquely consistent with the mechanism shown; both of the following schemes, for example, are consistent with the kinetic data:

II:
$$A + B \rightleftharpoons Y^- + H^+ + D \tag{5-48}$$
$$Y^- + H^+ + B \longrightarrow C + D \tag{5-49}$$

III:
$$A + B \rightleftharpoons U + V + D \tag{5-50}$$
$$U + V + B \longrightarrow C + D \tag{5-51}$$

They are kinetically indistinguishable from the original for a very good reason: the transition state for each step has the same composition in each of the three mechanisms given.

A particularly interesting aspect of sequential mechanism has been pointed out by Haim,[3] who used as an example published kinetic data[4] for the reaction

$$V^{3+} + Cr^{2+} = V^{2+} + Cr^{3+} \tag{5-52}$$

for which the rate expression is

$$\frac{-d[V^{3+}]}{dt} = \frac{q[V^{3+}][Cr^{2+}]}{r + [H^+]} \tag{5-53}$$

Two fundamentally different mechanisms† consistent with this expression can be formulated. Each has the correct activated complexes—namely $[CrV^{5+}]^{\ddagger}$ and $[VCrOH^{4+}]^{\ddagger}$—but differs in that the order of occurrence is reversed. The first mechanism invokes the formation of an intermediate $V(OH)Cr^{4+}$ from the hydrated cations by elimination of H^+, followed by a unimolecular reaction of the intermediate:

Mechanism I:
$$Cr^{2+} + V^{3+} + H_2O \underset{-1}{\overset{1}{\rightleftharpoons}} V(OH)Cr^{4+} + H^+ \tag{5-54}$$
$$V(OH)Cr^{4+} \xrightarrow{2} V^{2+} + CrOH^{2+} \tag{5-55}$$
$$CrOH^{2+} + H^+ \rightleftharpoons Cr^{3+} + H_2O \tag{5-56}$$

†Since $r = 0.108$ M and K_a for $V(H_2O)_6^{3+}$ is $\sim 2 \times 10^{-3}$ M, one need not consider mechanisms in which the two-term denominator arises from shifts in the acid ionization equilibrium. This point is elaborated upon in Sec. 5-6.

With the steady-state approximation the rate law becomes

$$\frac{-d[V^{3+}]}{dt} = \frac{(k_1 k_2/k_{-1})[Cr^{2+}][V^{3+}]}{(k_2/k_{-1}) + [H^+]} \tag{5-57}$$

which agrees with the experimental form. Haim points out, however, that a second and fundamentally quite different process† is also consistent with the data. In his alternative mechanism the two activated complexes occur in the opposite order, but the same intermediate is involved. The reactions are as follows.

Mechanism II:
$$V^{3+} + H_2O \rightleftharpoons VOH^{2+} + H^+ \quad \text{(rapid, } K_a\text{)} \tag{5-58}$$

$$VOH^{2+} + Cr^{2+} \underset{-3}{\overset{3}{\rightleftharpoons}} V(OH)Cr^{4+} \tag{5-59}$$

$$V(OH)Cr^{4+} + H^+ \xrightarrow{4} V^{2+} + Cr^{3+} + H_2O \tag{5-60}$$

which lead to the rate law

$$\frac{-d[V^{3+}]}{dt} = \frac{k_3 K_a[V^{3+}][Cr^{2+}]}{(k_{-3}/k_4) + [H^+]} \tag{5-61}$$

The chemistry of the two kinetically equivalent mechanisms is really rather different: in mechanism I the intermediate reacts unimolecularly to form products, whereas protonolysis returns it to the starting materials. Just the opposite is true in mechanism II.

To quote Haim: "Although the form of the rate law defines the composition of the activated complexes, the rate law does not specify (*a*) the order of formation of the activated complexes, (*b*) the species (reactants or intermediates) which generate the activated complexes, or (*c*) the decomposition products (intermediates or products) of the activated complexes."[3]

Newton and Baker[5] have suggested that a strong analogy is to be found between electrical circuits and reaction mechanisms. Birk[6] has amplified that notion. It will not be considered in great detail here, and the interested reader is referred to the indicated references. The Newton-Baker method consists of constructing an electrical circuit analogous to the mechanism; resistors correspond to activated complexes, junctions between resistors to steady-state intermediates, and terminals to reactants and products. *Any other electrical circuit which would give the same overall conductance corresponds to a kinetically equivalent mechanism.* These circuits correspond to *all* of the fundamentally different mechanisms.

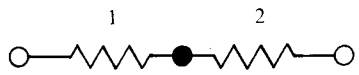
The electrical circuit corresponding to mechanism I for the V^{3+}-Cr^{2+} reaction,

†We shall not consider, as fundamentally different, sets of reaction steps which differ only in the mode of assembly of the same activated complex. Thus the following is not considered "different" from Eqs. (5-58) and (5-59) in the present context.

$$Cr^{2+} + H_2O \rightleftharpoons CrOH^+ + H^+ \tag{5-58a}$$

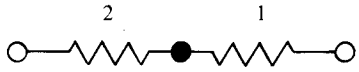
$$CrOH^+ + V^{3+} \underset{-3'}{\overset{3'}{\rightleftharpoons}} V(OH)Cr^{4+}(aq) \tag{5-59a}$$

which consists of a sequence of two activated complexes and one intermediate, is simply two resistances in series:



(5-62)

Clearly there is one (and only one) equivalent circuit, namely:



(5-63)

These arguments can be used to show that mechanisms I and II are the complete set of "fundamentally different" mechanisms which need be considered; we need not search for further possibilities. Having written one of the mechanisms, the electrical analog method would have told us that there was one other mechanism to be considered.

In the example at hand, both of the two mechanisms seem "reasonable," although perhaps chemical arguments might be advanced for one over the other. In some similar cases the second mechanism seems far less plausible. Consider, for example, the reaction of Fe^{2+} and Tl^{3+}, mentioned in Sec. 5-2. The mechanism shown in Eqs. (5-5) and (5-6) corresponds to the same circuit as in (5-62), and we therefore need to consider the alternative sequence corresponding to Eq. (5-63), in which the activated complexes occur in the reverse order. Such a mechanism is the following:

$$2Fe^{2+} \overset{K_1}{\rightleftharpoons} Fe^{+} + Fe^{3+} \qquad \text{(rapid, } K_1 \ll 1\text{)} \tag{5-64}$$

$$Fe^{+} + Tl^{3+} \underset{-1}{\overset{1}{\rightleftharpoons}} Fe^{2+} + Tl^{2+} \tag{5-65}$$

$$Fe^{3+} + Tl^{2+} \xrightarrow{2} Fe^{4+} + Tl^{+} \tag{5-66}$$

$$Fe^{4+} + Fe^{2+} = 2Fe^{3+} \qquad \text{(fast)} \tag{5-67}$$

which leads to the rate expression

$$\frac{-d[Tl^{3+}]}{dt} = \frac{(k_1 k_2 K_1 / k_{-1})[Fe^{2+}]^2 [Tl^{3+}]}{[Fe^{2+}] + (k_2 / k_{-1})[Fe^{3+}]} \tag{5-68}$$

The rate equation agrees with the experimental form [Eq. (5-4)]. However, the mechanism seems far less likely than that of Eq. (5-6), involving as it does two highly unusual and unstable oxidation states of iron.

5-6 PREEQUILIBRIA

We shall now examine the way in which a "balanced" or "partial" equilibrium affects the algebraic form of the rate law. We have already seen cases in which an equilibrium lay very far to one side or the other; the virtually complete ionization of HI made the

substitution $C_{HI} = [H^+] = [I^-]$ (Sec. 5-2) valid, and the trivial degree of formation of VOH^{2+} [Eq. (5-58)] or Fe^+ [Eq. (5-64)] gave simple expressions in terms of the concentrations of bulk reagents:

$$[VOH^{2+}] = \frac{K_a[V^{3+}]}{[H^+]} \quad \text{and} \quad [Fe^+] = \frac{K_1[Fe^{2+}]^2}{[Fe^{3+}]} \tag{5-69}$$

But the case in which the products and reactants of a mobile equilibrium are at comparable concentrations requires a separate treatment. For one thing it leads to a summation of denominator terms which have the same form as that for a successive-step mechanism, and one must take care to avoid an incorrect assignment. For another, it is necessary to have a rate law expressed in terms of the concentration of the predominant species in solution if the methods given earlier in this chapter are to be used to deduce the mechanism. To achieve that, proper account must be taken of all equilibrium steps which proceed to an appreciable extent.

Toward that end we first introduce some notation. The symbol C_i, or sometimes $[i]_T$, will be used to represent the *stoichiometric concentration*† of substance i; the *molar concentration* of the actual molecular or ionic species derived from substance i and in equilibrium with it are designated by the usual square brackets, and the values add to the total. Thus a dilute, acidic solution of chromium(VI) contains the species $HCrO_4^-$, $Cr_2O_7^{2-}$, and H_2CrO_4, and the following relation applies ,

$$C_{Cr(VI)} = [Cr(VI)]_T = [HCrO_4^-] + 2[Cr_2O_7^{2-}] + [H_2CrO_4] \tag{5-70}$$

It is useful to account for effects of such balanced equilibria in terms of the fractional degree of conversion of one species to the other. For an equilibrium written as a dissociation, such as the ionization of the weak acid HA, the relations are

$$\alpha_{HA} = \frac{[HA]}{C_A} = \frac{[H^+]}{K_a + [H^+]} \tag{5-71}$$

$$\alpha_A = 1 - \alpha_{HA} = \frac{[A^-]}{C_A} = \frac{K_a}{K_a + [H^+]} \tag{5-72}$$

Similarly, for an equilibrium written as an associative interaction, say, $M + L \rightleftharpoons ML$, the fractional distributions of M between the two forms are

$$\alpha_M = \frac{[M]}{C_M} = \frac{1}{1 + K[L]} \tag{5-73}$$

$$\alpha_{ML} = 1 - \alpha_M = \frac{[ML]}{C_M} = \frac{K[L]}{1 + K[L]} \tag{5-74}$$

The usual situation in kinetics is that the variable in *direct control* of the experimenter is the total amount of a substance added, such as C_A or C_M. The pertinent equilibria control the concentrations of the species present, and they must be used to convert the rate law from one containing stoichiometric concentrations to one con-

†Stoichiometric concentrations are termed by different workers as laboratory, analytical, formal, or total concentrations.

taining concentrations of species. The conversion is most conveniently accomplished by substitutions of the form shown in Eqs. (5-71) to (5-74).

By way of example, consider the decomposition of perbenzoic acid.

$$2C_6H_5CO_3H = 2C_6H_5CO_2H + O_2 \tag{5-75}$$

The mechanism[7] is proposed to consist of the bimolecular reaction of one molecule of the acid with a second of its conjugate base:

$$C_6H_5CO_3H \rightleftharpoons C_6H_5CO_3^- + H^+ \quad \text{(rapid, } pK_a = 7.78\text{)} \tag{5-76}$$

$$C_6H_5CO_3H + C_6H_5CO_3^- \xrightarrow{k_2} \text{products, or intermediate leading rapidly to products} \tag{5-77}$$

If [T] represents the total concentration of perbenzoic acid, the rate law of Eq. (5-78) is easily transformed to one expressed in terms of [T]:

$$\frac{d[O_2]}{dt} = k_2[C_6H_5CO_3H][C_6H_5CO_3^-] \tag{5-78}$$

$$\frac{d[O_2]}{dt} = \frac{k_2 K_a[H^+]}{(K_a + [H^+])^2}[T]^2 = k_{obs}[T]^2 \tag{5-79}$$

Equation (5-79) predicts a bell-shaped variation of log k_{obs} versus pH, maximizing at pH = pK_a, and indeed that is what is observed (Fig. 5-1). The shape of the curve

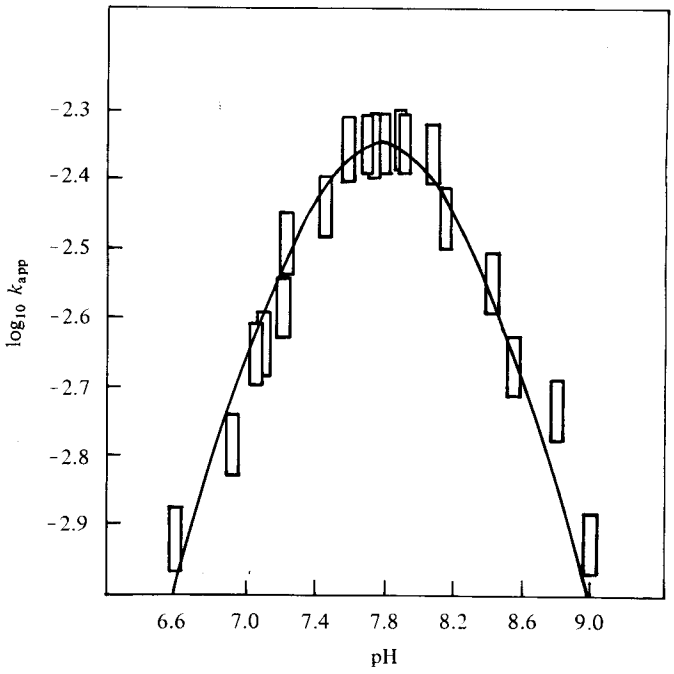


Figure 5-1 Rate-pH profile for the decomposition of peroxobenzoic acid at 25°. Data from Ref. 7.

and the seeming complexity arise from the protonation equilibrium. The actual mechanism is a simple one: bimolecular reaction of acid and base as shown in Eq. (5-77).

A second example will prove instructive, for it illustrates the point that in many circumstances a rate law written in terms of stoichiometric concentrations has the same mathematical form as the rate law applicable to a sequential reaction mechanism.

Taube and Posey[8] found that the rate of the reaction

$$Co(NH_3)_5H_2O^{3+} + SO_4^{2-} = Co(NH_3)_5SO_4^{+} + H_2O \tag{5-80}$$

followed pseudo-first-order kinetics in the presence of a large excess of sulfate ions. Above 0.02 M SO_4^{2-}, however, the rate became independent of $[SO_4^{2-}]$ in accord with the equation

$$\frac{d[Co(NH_3)_5SO_4^{+}]}{dt} = \frac{A[SO_4^{2-}][Co(NH_3)_5H_2O^{3+}]}{1 + B[SO_4^{2-}]} \tag{5-81}$$

Now, if an ion-pairing equilibrium had gone unrecognized, Eq. (5-81) could have been (incorrectly) interpreted in terms of a limiting S_N1 mechanism in which a five-coordinate intermediate $Co(NH_3)_5^{3+}$ plays a major role:

$$Co(NH_3)_5OH_2^{3+} \underset{-1}{\overset{1}{\rightleftharpoons}} Co(NH_3)_5^{3+} + H_2O, \tag{5-82}$$

$$Co(NH_3)_5^{3+} + SO_4^{2-} \xrightarrow{2} Co(NH_3)_5SO_4^{+} \tag{5-83}$$

This formulation is consistent with the experimental equation, with $A = k_1k_2/k_{-1}$ and $B = k_2/k_{-1}$.

In fact, the effect arises from an entirely different phenomenon. Taube and Posey recognized that the reactants associate to an outer-sphere complex or ion pair according to the reaction

$$Co(NH_3)_5H_2O^{3+} + SO_4^{2-} \overset{K_{IP}}{\rightleftharpoons} Co(NH_3)_5H_2O^{3+}\cdot SO_4^{2-} \tag{5-84a}$$

$$[Co(NH_3)_5H_2O^{3+}\cdot SO_4^{2-}] \xrightarrow{k_3} Co(NH_3)_5SO_4^{+} + H_2O \tag{5-84b}$$

This alters the interpretation, because the experimental rate constant of Eq. (5-81) is (automatically) expressed in terms of total cobalt and must be converted to an expression involving the concentrations of species. Substitution of the relation

$$\frac{[Co(NH_3)_5H_2O^{3+}\cdot SO_4^{2-}]}{[Co]_T} = \frac{K_{IP}[SO_4^{2-}]}{1 + K_{IP}[SO_4^{2-}]} \tag{5-85}$$

yields the equivalent kinetic expressions

$$\frac{d[Co(NH_3)_5SO_4^{+}]}{dt} = A[Co(NH_3)_5H_2O^{3+}][SO_4^{2-}] \tag{5-86a}$$

$$\frac{d[Co(NH_3)_5SO_4^{+}]}{dt} = \frac{A}{K_{IP}}[Co(NH_3)_5H_2O^{3+}\cdot SO_4^{2-}] \tag{5-86b}$$

and identifies parameter B of Eq. (5-81) as K_{IP}. This new rate law, which expresses the rate in terms of the concentrations of species present in solution, no longer displays the feature of the limiting rate in SO_4^{2-}.

Thus we see the difference between the situation in which an association or dissociation equilibrium converts a *significant* fraction of the reactant into a different form, one which may be more or less reactive than the original, and the case in which only a minute fraction is converted to *highly reactive* form. These cases, of quite great mechanistic difference, often lead to rate laws of the same algebraic form. In general, one must be able to determine the quantitative extent of the interaction to distinguish between the alternatives. Experiments having higher concentrations of cobalt complex would have served to distinguish the possibilities. In these experiments, if the ion-pairing mechanism holds, $[SO_4^{2-}]$ can no longer be approximated as $[SO_4^{2-}]_T$, whereas the relation remains valid for the S_N1 mechanism if no appreciable quantity of ion pair forms. There may well be practical limitations to the application of this method, however, arising from the more complex analysis required for the kinetic data during each run where an irreversible pseudo-first-order relation will no longer apply.

Still further consideration of this reaction may be instructive. Suppose that the mechanism *were* the S_N1 process, with the dissociative reaction (5-82) rate-limiting and (5-83) quite fast ($k_2[SO_4^{2-}] \gg k_{-1}$). Suppose also that the ion-pairing equilibrium of (5-84*a*) were important but nonproductive (i.e., the ion pair forms to an extent given by this equilibrium, but it is nonreactive, $k_3 = 0$). In this case it is easily shown, for experiments having a large excess of sulfate ions, that

$$\frac{d[Co(NH_3)_5SO_4^+]}{dt} = \frac{k_1[Co(NH_3)_5H_2O^{3+}]_T[SO_4^{2-}]}{1 + K_{IP}[SO_4^{2-}]}$$

The fact that the coefficient of the sulfate ion term in the denominator would have the numerical value given by an independent determination of K_{IP} can be seen from this equation to be neither coincidental nor indicative of a key role of ion pairing in the mechanism. It merely reflects, in this case, the extent of conversion of the cobalt complex to what is presumed in this mechanism to be a nonreactive storage point.

Consider once again the mechanism of the reaction between V^{3+} and Cr^{2+}, Eqs. (5-52) and (5-53). One might argue for a mechanism far simpler than those proposed in mechanisms I and II. For example, consider the following possibility:

$$V^{3+} + H_2O \rightleftharpoons VOH^{2+} + H^+ \quad \text{(rapid, } K_a\text{)} \tag{5-87}$$

$$VOH^{2+} + Cr^{2+} \xrightarrow{k_s} CrOH^{2+} + V^{2+} \tag{5-88}$$

$$CrOH^{2+} + H^+ = Cr^{3+} + H_2O \tag{5-89}$$

Accounting for a distribution of vanadium(III) between the two forms,

$$[VOH^{2+}] = \frac{[V(III)]_T K_a}{(K_a + [H^+])} \tag{5-90}$$

the rate law associated with this mechanism is

$$\frac{d[V^{2+}]}{dt} = k_5[VOH^{2+}][Cr^{2+}] \tag{5-91}$$

$$\frac{d[V^{2+}]}{dt} = \frac{k_5 K_a [V(III)]_T [Cr^{2+}]}{[H^+] + K_a} \tag{5-92}$$

This form is *algebraically* equivalent to that observed experimentally, with $q = k_5 K_a$ and $r = K_a$. The basis for discarding the mechanism is that the experimental value of r (0.108 M) and the known value of K_a ($\sim 2 \times 10^{-3}$ M) agree far too poorly to be reconciled. Discarding the mechanism does not, of course, preclude the involvement of VOH^{2+} as the reactive species in other, possibly correct, mechanisms, such as that given earlier in mechanism II (page 100)

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PROBLEMS

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

Scheme I:

$$Tl^{3+} + Fe^{2+} \underset{-1}{\overset{1}{\rightleftharpoons}} Tl^{2+} + Fe^{3+}$$

$$Tl^{2+} + Fe^{2+} \xrightarrow{2} Tl^+ + Fe^{3+}$$

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

Scheme II:

$$Tl^{3+} + Fe^{2+} \underset{-3}{\overset{3}{\rightleftharpoons}} Tl^+ + Fe^{4+}$$

$$Fe^{4+} + Fe^{2+} \xrightarrow{4} 2Fe^{3+}$$

Scheme III:

$$2Fe^{2+} \rightleftharpoons Fe^+ + Fe^{3+} \quad (K_5 \ll 1)$$

$$Fe^+ + Tl^{3+} \underset{-6}{\overset{6}{\rightleftharpoons}} Fe^{2+} + Tl^{2+}$$

$$Fe^{3+} + Tl^{2+} \xrightarrow{7} Fe^{4+} + Tl^+$$

$$Fe^{4+} + Fe^{2+} = 2Fe^{3+} \quad \text{(very fast)}$$

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

$$[Ni(cp)_2(CO)_2] \underset{-1}{\overset{1}{\rightleftharpoons}} [Ni(cp)_2(CO)_2]^*$$

$$[Ni(cp)_2(CO)_2]^* + PhCCPh \xrightarrow{2} [Ni(cp)_2(PhCCPh)] + 2CO$$

$$\text{Net:} \quad [Ni(cp)_2(CO)_2] + PhCCPh = [Ni(cp)_2(PhCCPh)] + 2CO$$

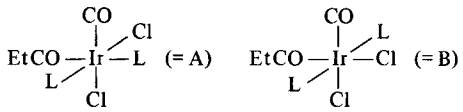
in which $[Ni(cp)_2(CO)_2]^*$ represents a steady-state intermediate of rearranged structure.

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

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

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

$$2Me_3SiEt = Me_2SiEt_2 + Me_4Si$$

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

$$\frac{-d[Me_3SiEt]}{dt} = \frac{\alpha[Me_3SiEt]^2[Al_2Br_6]}{1 + \beta[Me_3SiEt]}$$

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

$$2V(III) + 2Hg(II) = 2V(IV) + [Hg(I)]_2$$

has a rate term showing the following concentration dependences

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

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

$$V(III) + V(V) \longrightarrow 2V(IV) \qquad Hg(II) + Hg^0 \longrightarrow [Hg(I)]_2$$

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

$$Co_2(CO)_8 + RC_2R' = Co_2(CO)_6RC_2R' + 2CO$$

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:

Mechanism I:

$$Co_2(CO)_8 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Co_2(CO)_7 + CO$$

$$Co_2(CO)_7 + Ph_2C_2 \xrightarrow{k_2} Co_2(CO)_6Ph_2C_2 + CO$$

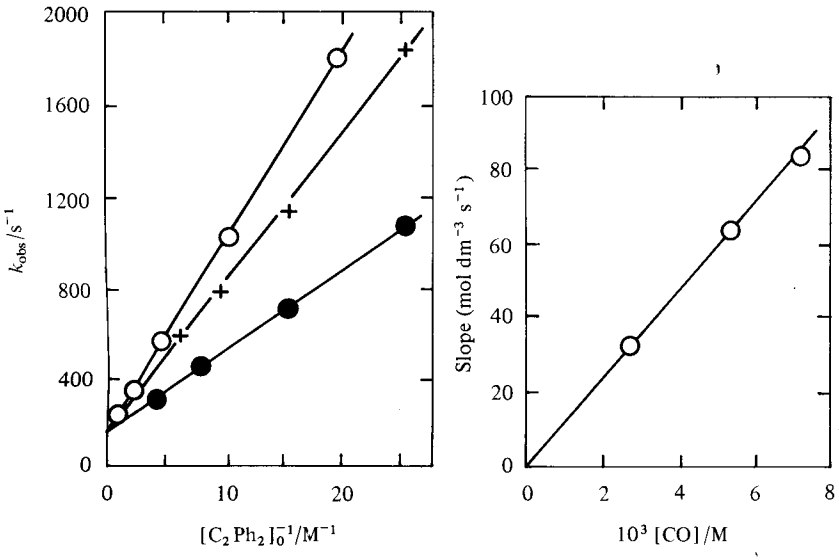
Mechanism II:

$$Co_2(CO)_8 + Ph_2C_2 \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} Co_2(CO)_7Ph_2C_2 + CO$$

$$Co_2(CO)_7Ph_2C_2 \xrightarrow{k_4} Co_2(CO)_6Ph_2C_2 + CO$$

(*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:

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

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.

5-8 *Rate law and mechanism.* Propose a mechanism for each and relate the parameters of the rate law to the rate constants for the mechanism.

(*a*) The hydrolysis of benzhydryl chloride in aqueous acetone,

$$Ph_2CHCl + H_2O = Ph_2CHOH + Cl^- + H^+; \frac{d[Ph_2CHOH]}{dt} = \frac{\alpha[Ph_2CHCl]}{\beta + [Cl^-]}$$

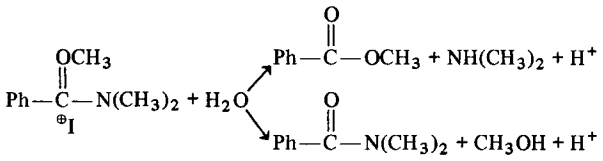
(*b*) The oxidation of iodide by aqueous Fe^{3+}, $2Fe^{3+} + 3I^- = 2Fe^{2+} + I_3^-$,

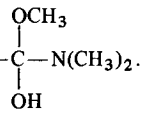
$$\frac{-d[Fe^{3+}]}{dt} = \frac{k[Fe^{3+}]^2[I^-]^2}{[Fe^{3+}] + k'[Fe^{2+}]}$$

(*c*) Smith and Yates [*J. Am. Chem. Soc.*, 94:8811 (1972)] find that the hydrolysis of trimethylbenzimidate (I) follows the rate law

$$\frac{-d[I]}{dt} = \frac{A + B/[H^+]}{1 + C[H^+]}[I]$$

At low $[H^+]$ the products are primarily amine plus ester, whereas at high $[H^+]$, amide and alcohol are formed:



Hint: Consider parallel reactions of the intermediate  .

5-9 *Mechanistic distinction and interpretations; preequilibria.* The oxidation of I^- by $HCrO_4^-$ is *catalyzed by* oxalic acid. Vandegrift and Rocek [*J. Am. Chem. Soc.*, 98:1372 (1976)] have carried out studies under conditions in which $[HCrO_4^-] \ll [H^+]$, $[I^-]$, and $[(COOH)_2]$. The rate is first-order in Cr(VI), $-d[Cr(VI)]/dt = k_{cat}[Cr(VI)]$.

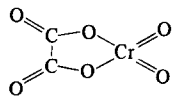
The authors formulate two alternative mechanisms: I, in which a rapid and reversible equilibrium converts a significant portion of $HCrO_4^-$ to $ICrO_3^-$, and II, in which Cr(VI) exists only as $HCrO_4^-$ and reacts in a two-step sequence involving a steady-state oxalochromate intermediate. Derive the rate law for each mechanism. A plot of $1/k_{cat}$ versus $1/[I^-]$ (at constant $[(COOH)_2]$ and $[H^+]$) is linear, with intercept designated $1/A$ and intercept/slope = B. The data are shown below; interpret in terms of schemes I and/or II.

Scheme I:

$$HCrO_4^- + I^- + H^+ \overset{K_1}{\rightleftharpoons} ICrO_3^- + H_2O$$

$$ICrO_3^- + (CO_2H)_2 \xrightarrow{2} \text{products}$$

Scheme II:

$$HCrO_4^- + (CO_2H)_2 + H^+ \underset{-3}{\overset{3}{\rightleftharpoons}} \text{  } + 2H_2O$$

$$(CO_2)_2CrO_2 + I^- \xrightarrow{4} \text{products}$$

$[H^+]$	$10^3[(CO_2H)_2]$	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.

$$2Fe^{II}L + I_3^- = 2Fe^{III}L + 3I^-$$

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

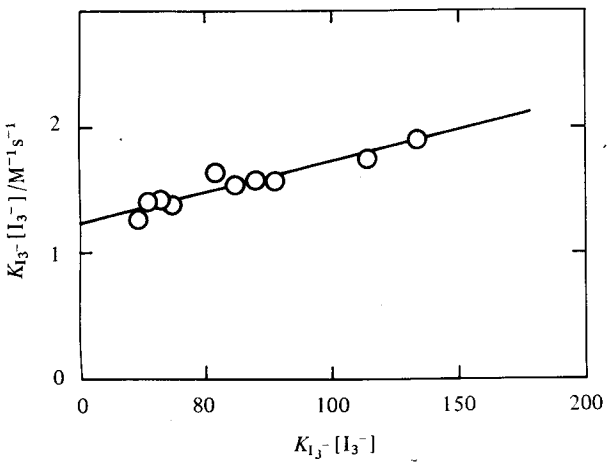
$$\frac{-d[I_2]_T}{dt} = k_0[Fe^{II}L][I_2]_T$$

A correction was applied for the equilibrium

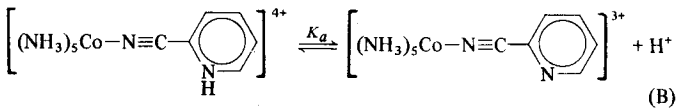
$$I_2 + I^- \rightleftharpoons I_3^- \qquad (K_{I_3} = 770\ M^{-1} \text{ at } 25°)$$

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°.

$$Fe^{II}L \xrightarrow[I_2]{k_1} IFe^{III}L + I\cdot$$
$$Fe^{II}L \xrightarrow[I_3^-]{k_2} IFe^{III}L + I_2^-\cdot$$



5-11 *Preequilibria.* The reactions of cyanopyridine complexes of cobalt(III) with chromium(II) have been studied [*J. Am. Chem. Soc.*, 98:1487 (1976)]. The reactions are complicated by a protonation



(B)

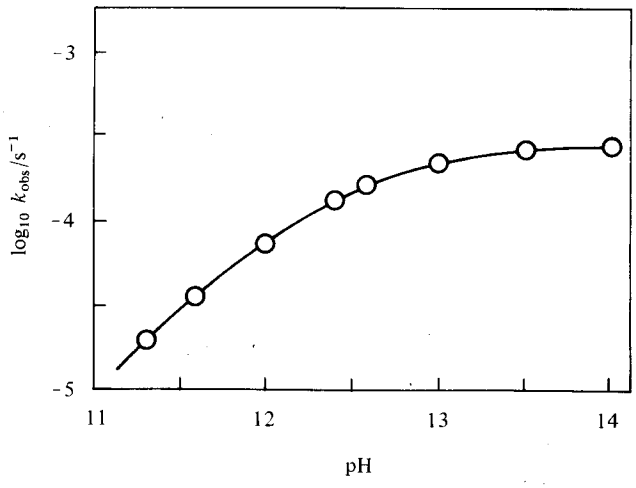
Derive the rate expression for $-d[\text{Co(III) complex}]/dt$ in these cases: (*a*) The 2-cyanopyridine complex shown, in which only the basic form reacts with Cr^{2+}, $B_2 + Cr^{2+} \xrightarrow{k_1}$ products, and (*b*) The analogous 3-cyanopyridine complex in which parallel reaction of acid and base occur: $A_3 + Cr^{2+} \xrightarrow{k_2}$ products and $B_3 + Cr^{2+} \xrightarrow{k_3}$ products.

5-12 *Preequilibria.* Biechler and Taft [*J. Am. Chem. Soc.*, 79:4932 (1957)] have studied the base hydrolysis of trifluoroacetanalide, a reaction which is complicated by an acid-base equilibrium:

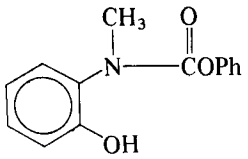
Net reaction: $$CF_3\overset{\overset{O}{\|}}{C}NPhH + OH^- = CF_3CO_2^- + PhNH_2$$

Acid base: $$CF_3CONPhH \rightleftharpoons CF_3CONPh^- + H^+ \qquad pK_a = 12.43$$

The reaction is pseudo-first-order in the total concentration of reactant, and shows the pH profile depicted. Give a complete mechanistic interpretation.

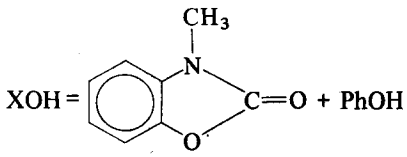


5-13 *Preequilibria.* Hutchins and Fife [*J. Am. Chem. Soc.*, 95:2282 (1973)] have shown that carbamate XOH undergoes an instantaneous acid-base equilibrium



$$(XOH) \rightleftharpoons XO^- + H^+ \quad (K_a = 1.0 \times 10^{-9})$$

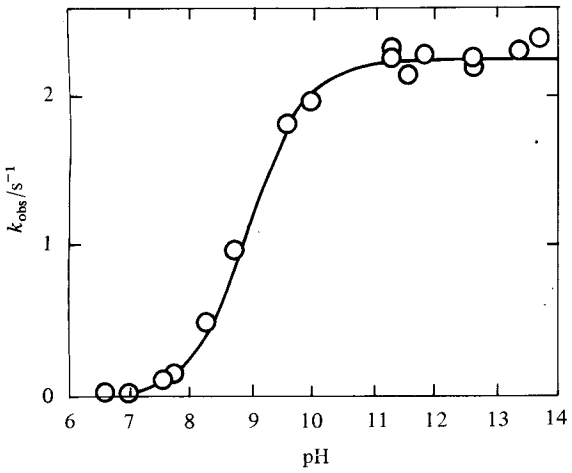
but is susceptible to decomposition:



Give a quantitative interpretation of the kinetic data. The rate law is given by

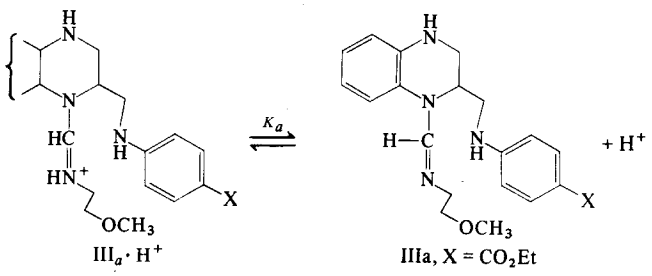
$$\frac{d[\text{PhOH}]}{dt} = k_{\text{obs}}[X]_T$$

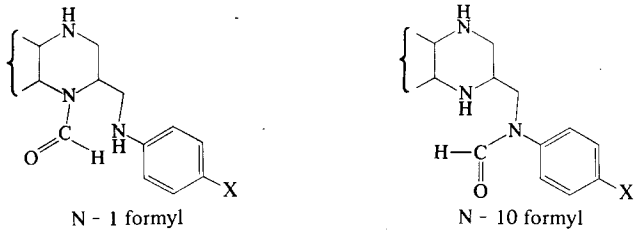
where $[X]_T = [XOH] + [XO^-]$, and the pH profile is as shown.



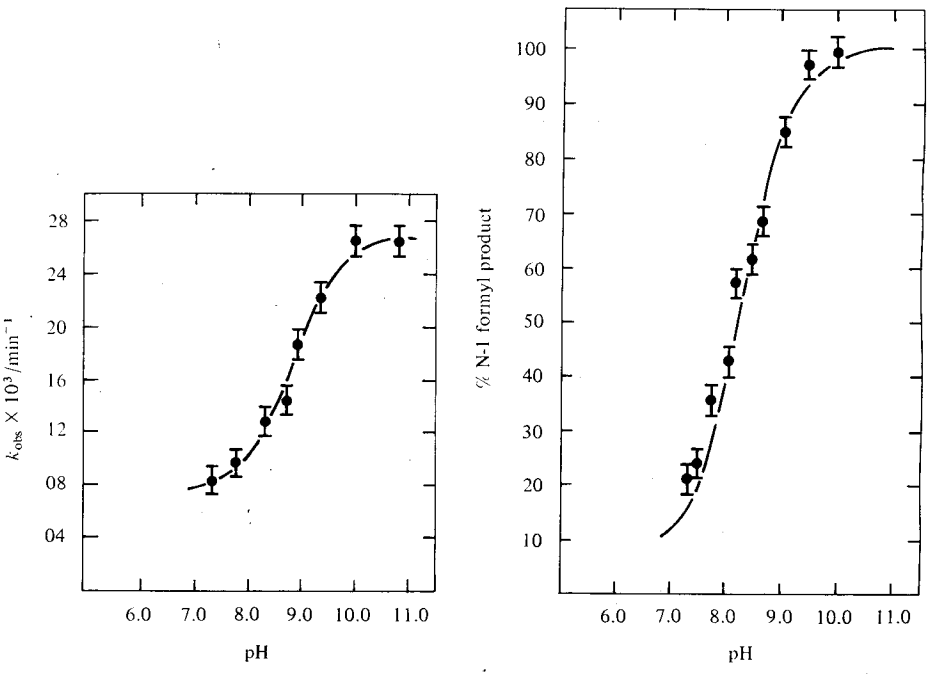
5-14 *Composite rate constants.* Give the expression by which k_4 of Eq. (5-20) can be calculated from the constants of Eqs. (5-15) to (5-19).

5-15 *Preequilibria and product distribution.* Benkovic et al. [*J. Am. Chem. Soc.*, 95:8414 (1973)] have studied the hydrolysis of formamide III*a* to a mixture of N-1 and N-10 formyl products; the reactant is involved in an ionization equilibrium ($K_a = 2 \times 10^{-9}$ M):





They evaluate the pseudo-first-order rate constant and the percentage yield of N-1 product both as functions of pH, obtaining data depicted below. Propose a mechanism; show that it accounts for these results; and evaluate all possible rate constants.



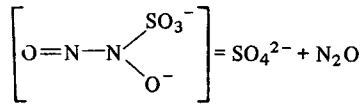
5-16 *Preequilibria and rate law.* The rate of isotopic exchange between U(IV) and U(VI) follows a second-order rate expression at constant $[H^+]$:

$$R_{ex} = k_{ex}[U(VI)][U(IV)]_T$$

where $[U(IV)]_T = [U^{4+}] + [UOH^{3+}]$, related by the equilibrium $U^{4+} + H_2O = UOH^{3+} + H^+$, $K_a = 5.6 \times 10^{-2}$ mol dm^{-3}. The only U(VI) species in the pH range considered is UO_2^{2+}. Using the data provided [from Schwartz and Masters, *J. Am. Chem. Soc.*, 83:2620 (1961)], express the exchange rate as a function of $[UO_2^{2+}]$, $[U^{4+}]$, and $[H^+]$, and compute the rate constant(s) of this equation.

$[H^+]$/mol dm^{-3}	0.200	0.100	0.0500	0.0250
k_{ex}/dm^3 mol^{-1} s^{-1}	2.05×10^{-5}	1.34×10^{-4}	7.92×10^{-4}	4.15×10^{-3}

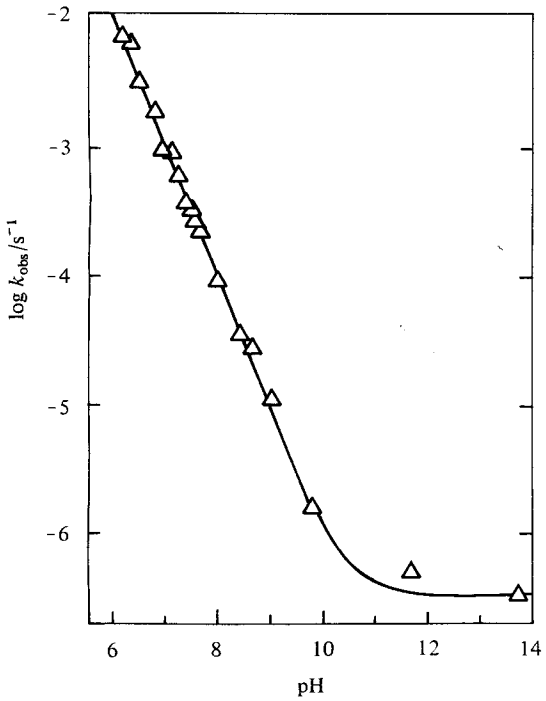
5-17 *pH profile and reaction mechanism.* Switkes, Dasch, and Ackerman [*Inorg. Chem.*, 12:1120 (1973)] have studied the decomposition of *N*-nitrosohydroxylamine-*N*-sulfonate ion (= X^{2-}).



$$= SO_4^{2-} + N_2O$$

The rate law follows the expression

$$\frac{-d[X^{2-}]}{dt} = k_{obs}[X^{2-}]$$



The pH profile at 25°C is shown. The equilibrium $HX^- = X^{2-} + H^+$ has $K_a = 1.0 \times 10^{-2}$ mol dm^{-3}. Formulate a mechanism consistent with these data.

5-18 *Reaction mechanism.* Interpret the following data as completely as possible. S. J. Okrasinski and J. R. Norton [*J. Am. Chem. Soc.*, 99:295 (1977)] have studied two reactions of $HOs(CO)_4CH_3$, thermolysis(1) and reaction with phosphine(2):

1: $$2HOs(CO)_4CH_3 = CH_4 + HOs(CO)_4Os(CO)_4CH_3$$

2: $$HOs(CO)_4CH_3 + PR_3 = CH_4 + Os(CO)_4PR_3$$

The reaction rates at 49°C in methylcyclohexane are:

Thermolysis: $$\frac{-d[HOs(CO)_4CH_3]}{dt} = k_1[HOs(CO)_4CH_3]$$

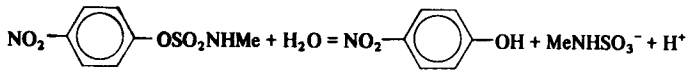
$$k = (1.38 \pm 0.06) \times 10^{-4}\ s^{-1}$$

Phosphine: $$\frac{-d[HOs(CO)_4CH_3]}{dt} = k_2[HOs(CO)_4CH_3]$$

$$k_2 = (6.4 \pm 0.1) \times 10^{-5}\ s^{-1}$$

A mixture of $HOs(CO)_4CD_3$ and $DOs(CO)_4CH_3$, in either thermolysis or reaction with phosphine, yields a mixture of CD_3H and CH_3D, but no CD_4 or CH_4.

5-19 *pH depenedence.* Williams and Douglas [*J. Chem. Soc. Perkin II*, 1727 (1974)] have studied the kinetics of the following hydrolysis reaction:



The starting material undergoes acid dissociation with pK_a 8.9; the reaction proceeds by parallel hydrolysis of acid ($k_1 = 4 \times 10^{-6}\ s^{-1}$) and anion ($k_2 = 8 \times 10^{-3}\ s^{-1}$). Sketch the expected pH profile showing the important features semiquantitatively with numerical scales on the axes.