TABLE III

SPECTRA AT 400–4000 CM^{-1}

$((C_6H_5)_3P_3CuSnCl_3$	$((C_6H_5)_3P)_3AgSnCl_3$	$((C_6H_5)_3P)_3AuSnCl_3$
445 m	443 m	445 m
494 s	489 s	491 s
502 s	501 s	502 s
516 s	515 s	515 s
619 w	618 w	...
660 m, sh	668 m, sh	670 m, sh
695 s	695 s	695 s
725 m	724 m	722 m
745 s	745 s	745 s
755 m, sh	755 m, sh	755 m, sh
850 m	847 m	850 w
998 m	1000 m	995 m
1015 w	1025 w	1025 w
1090 m	1090 m	1092 m
1160 w	1162 w	1155 w
1180 w	1185 w	1170 w
1223 w	1226 w	1221 w
1311 w	1312 w	1309 w
1722 w	1721 w	1720 m

distorted tetrahedron. While four-coordinate complexes of copper and silver are common, the corresponding compounds of Au(I) are rarer. It is interesting to note that Glockling and Hooton[3] were unable to prepare $[(C_6H_5)_3P]_3AuGe(C_6H_5)_3$, although the copper and silver complexes were isolated. The occurrence of maximum coordination in these systems is probably due to d_π–d_π bonding between the central metal and the phosphorus and tin which prevents a buildup of electron density on the metal.

From the infrared data given in Table II it can be seen that the $SnCl_3$ stretching frequencies increase upon coordination to a Lewis acid. For a series of Pt(II) complexes, Parshall[8] reported that a doublet in the infrared spectra at 330 cm^{-1} is characteristic of σ-bonded $SnCl_3$. In our compounds two $SnCl_3$ vibrations are observed at *ca.* 290 and 310 cm^{-1}. By analogy with $SnCl_3^-$ and $SnCl_3BF_3^-$, these bands have been assigned to the symmetric and asymmetric stretching modes of $SnCl_3$. The appearance of two bands is consistent with the local C_{3v} symmetry about the tin atom.

Johnson and Shriver[9] have shown that there is a correlation between the $SnCl_3$ stretching frequencies and the oxidation state of a given acid in mononuclear compounds. As shown in Table II the frequencies for complexes containing a metal in the +1 oxidation state occur between the values for free $SnCl_3^-$ and the Pt(II) complexes of $SnCl_3$.

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(8) R. V. Lindsey, Jr., G. W. Parshall, and U. G. Stolberg, *Inorg. Chem.*, **6**, 109 (1966).

(9) M. P. Johnson and D. F. Shriver, unpublished results.

Correspondence

The Ambiguity of Mechanistic Interpretations of Rate Laws: Alternate Mechanisms for the Vanadium(III)-Chromium(II) Reaction[1]

Sir:

Although some of the features of the mechanism of a reaction can be established from kinetic data, it is well known that such data are usually insufficient to derive a complete and unique mechanism. The mechanistic information contained in a rate law has been expressed in terms of the composition of the activated complex[2,3] or, alternately, in terms of the net activation process.[4] Beyond this, what is usually done is to propose various mechanisms *consistent* with the observed rate law and, with the aid of additional considerations, to choose the most "reasonable" mechanism.

In going from rate laws to mechanisms, two related questions may be raised. First, how is a complete set of mechanisms derived from an experimental rate law? Second, given a set of kinetically indistinguishable mechanisms, what classes of mechanistic ambiguities can be discerned? Neither of these questions has been treated systematically in the published literature.[5] However, Newton[6] has developed an elegant method, based on electrical analogs of reaction paths, to obtain a complete set of mechanisms consistent with a given rate law. Furthermore, Newton[6] has discussed, in a general manner, various levels of mechanistic ambiguities.

One type of mechanistic ambiguity, exemplified by the ammonia–cyanic acid reaction,[7] has been recognized for a long time. Since the rate law defines the composition of the activated complex but not the species from which it is generated, various mechanisms can be devised when the rate-determining step is preceded by rapid equilibria.[2,3,7] Such ambiguities can be circumvented, although not eliminated, by making use of the concept of net activation process.[4]

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(1) This work was supported by Grant GP-2001 from the National Science Foundation.

(2) E. L. King in "Catalysis," P. H. Emmett, Vol. II, Reinhold Publishing Corporation, New York, N. Y., 1955, p 337.

(3) H. Taube, *J. Chem. Educ.*, **36**, 451 (1959).

(4) T. W. Newton and S. W. Rabideau, *J. Phys. Chem.*, **62**, 943 (1958).

(5) Some general comments about the mechanistic significance of rate laws can be found in ref 2.

(6) T. W. Newton, private communication.

(7) See, for example, I. Weil and J. C. Morris. *J. Am. Chem. Soc.*, **71**, 1664 (1949).

A second type of ambiguity,[6] which apparently has not been discussed in the literature, can obtain in reactions that proceed *via* two consecutive activated complexes. This ambiguity comes about because the form of the rate law specifies the compositions of the activated complexes but not the sequence in which they are formed. A recent study[8] of the vanadium(III)–chromium(II) reaction provides an interesting example of this type of ambiguity.

The rate law for the reaction was reported[8] to be

$$\text{rate} = \frac{q[\mathrm{V^{3+}}][\mathrm{Cr^{2+}}]}{r + [\mathrm{H^+}]} \qquad (1)$$

As will be seen later, the form of this rate law has been challenged.[9] Nevertheless, it appears useful to inquire about the mechanistic significance of eq 1. The limiting forms of eq 1 at low and high $[\mathrm{H^+}]$ are $q[\mathrm{V^{3+}}][\mathrm{Cr^{2+}}]/r$ and $q[\mathrm{V^{3+}}][\mathrm{Cr^{2+}}]/[\mathrm{H^+}]$, respectively. The compositions of the corresponding activated complexes are $\mathrm{VCr^{5+}}$ and $\mathrm{V(OH)Cr^{4+}}$, indicating, according to the proposed[8] interpretation, the reaction of $\mathrm{V^{3+}}$ with $\mathrm{Cr^{2+}}$ and the spontaneous aquation of the binuclear complex $\mathrm{V(OH)Cr^{4+}}$, respectively. The proposed mechanism[8,10]

Mechanism I

$$\mathrm{V^{3+} + Cr^{2+} + H_2O \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} V(OH)Cr^{4+} + H^+} \qquad (2)$$

$$\mathrm{V(OH)Cr^{4+} \xrightarrow{k_2} V^{2+} + CrOH^{2+}} \qquad (3)$$

$$\mathrm{CrOH^{2+} + H^+ \rightleftharpoons Cr^{3+} + H_2O} \quad \text{(rapid)} \qquad (4)$$

yields the relation

$$\text{rate} = \frac{k_1k_2[\mathrm{V^{3+}}][\mathrm{Cr^{2+}}]}{k_2 + k_{-1}[\mathrm{H^+}]} \qquad (5)$$

which is seen to have a form identical with that of eq 1. The values (25°) of k_1 and k_2/k_{-1}, derived from the empirical parameters q and r, are 5.76 M^{-1} sec^{-1} and 0.108 M, respectively.[8]

We wish to propose an alternate mechanistic interpretation for the activated complexes of composition $\mathrm{V(OH)Cr^{4+}}$ and $\mathrm{VCr^{5+}}$. The former corresponds to the reaction of the hydrolyzed species $\mathrm{VOH^{2+}}$ with $\mathrm{Cr^{2+}}$. The activated complex $\mathrm{CrV^{5+}}$ can be cast in the equivalent form $\mathrm{V(OH)Cr^{4+} + H^+}$ and suggests the reaction of the binuclear intermediate $\mathrm{V(OH)Cr^{4+}}$ with $\mathrm{H^+}$. The alternate mechanism

Mechanism II

$$\mathrm{V^{3+} + H_2O \rightleftharpoons VOH^{2+} + H^+} \quad (\text{rapid}, Q) \qquad (6)$$

$$\mathrm{VOH^{2+} + Cr^{2+} \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} V(OH)Cr^{4+}} \qquad (7)$$

$$\mathrm{V(OH)Cr^{4+} + H^+ \xrightarrow{k_4} V^{2+} + Cr^{3+} + H_2O} \qquad (8)$$

leads to the relation

$$\text{rate} = \frac{k_3k_4Q[\mathrm{V^{3+}}][\mathrm{Cr^{2+}}]}{k_{-3} + k_4[\mathrm{H^+}]} \qquad (9)$$

Equation 9 has a form identical with that derived from mechanism I (eq 5) and with the empirical rate law (eq 1). Using the parameters q and r given by Espenson,[8] we calculate the following constants (25°): $k_3 = 3.12 \times 10^2\ M^{-1}$ sec^{-1} and $k_{-3}/k_4 = 0.108\ M$.

Mechanisms I and II illustrate the ambiguity indicated above, namely that the form of the rate law does not define the order of formation of the activated complexes. In mechanism I the acid-independent term $[\mathrm{VCr^{5+}}]^*$ comes earlier than the acid-dependent term $[\mathrm{V(OH)Cr^{4+}}]^*$, whereas the opposite order obtains for mechanism II.[11] Moreover, it is interesting to note that the acid-independent term of mechanism II arises from the fact that a proton is first *subtracted* from $\mathrm{V^{3+}}$ (eq 6) and then *added* to the postulated binuclear intermediate $\mathrm{V(OH)Cr^{4+}}$ (eq 8).

In the previous discussion we have assumed that the empirical relation (eq 1) proposed by Espenson[8] adequately describes the observed dependence of rate upon $[\mathrm{H^+}]$. Recently, Sykes[9] took issue with the form of the rate law chosen by Espenson and suggested that a better fit of the data is obtained by using the empirical rate law

$$\text{rate} = \frac{a + b[\mathrm{H^+}]^{-1}}{c + [\mathrm{H^+}]}[\mathrm{V^{3+}}][\mathrm{Cr^{2+}}] \qquad (10)$$

The proposed mechanism[9]

Mechanism III

$$\mathrm{V^{3+} + Cr^{2+} + H_2O \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} V(OH)Cr^{4+} + H^+} \qquad (2)$$

$$\mathrm{VOH^{2+} + Cr^{2+} \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} V(OH)Cr^{4+}} \qquad (7)$$

$$\mathrm{V(OH)Cr^{4+} \xrightarrow{k_2} V^{2+} + CrOH^{2+}} \qquad (3)$$

leads to the relation

$$\text{rate} = \frac{k_1k_2 + k_2k_3Q[\mathrm{H^+}]^{-1}}{(k_2 + k_{-3}) + k_{-1}[\mathrm{H^+}]}[\mathrm{V^{3+}}][\mathrm{Cr^{2+}}] \qquad (11)$$

From the parameters a, b, and c (eq 10) given by Sykes,[9] the following constants (25°) can be obtained: $k_1k_2/k_{-1} = 0.67$ sec^{-1}, $k_2k_3/k_{-1} = 3.7$ sec^{-1}, $(k_2 + k_{-3})/k_{-1} = 0.16\ M$, and $k_3/k_1 = 5.4$.

Mechanism III features three activated complexes of composition $[\mathrm{VCr^{5+}}]^*$, $[\mathrm{V(OH)Cr^{4+}}]^*$, and $[\mathrm{V(OH)Cr^{4+}}]^*$, respectively. The two activated complexes of the same composition differ in the way they are formed. One originates in the reactants (eq 7), whereas the other originates in the intermediate (eq 3). A similar situation was previously observed in the $\mathrm{PuO_2^{2+}}$–$\mathrm{Fe^{2+}}$ reaction.[12]

We wish to propose an alternate mechanism consistent with the empirical rate law suggested by Sykes.

Mechanism IV

$$\mathrm{VOH^{2+} + Cr^{2+} \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} V(OH)Cr^{4+}} \qquad (7)$$

$$\mathrm{V(OH)Cr^{4+} \xrightarrow{k_2} V^{2+} + CrOH^{2+}} \qquad (3)$$

$$\mathrm{V(OH)Cr^{4+} + H^+ \xrightarrow{k_4} V^{2+} + Cr^{3+} + H_2O} \qquad (8)$$

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[8] J. H. Espenson, *Inorg. Chem.*, **4**, 1025 (1965).

[9] A. G. Sykes, *Chem. Commun.*, 442 (1965).

[10] For simplicity we use the formulation with $n = 1$.

[11] There is an interesting correlation between mechanisms I and II. Mechanism II is entirely analogous to the mechanism for the reverse of the V(III)–Cr(II) reaction predicted on the basis of mechanism I and microscopic reversibility considerations.

[12] T. W. Newton and F. B. Baker, *J. Phys. Chem.*, **67**, 1425 (1963).

The rate law derived from mechanism IV is

$$\text{rate} = \frac{k_3k_4Q + k_2k_3Q[\text{H}^+]^{-1}}{(k_2 + k_{-3}) + k_4[\text{H}^+]}[\text{V}^{3+}][\text{Cr}^{2+}] \qquad (12)$$

The form of eq 12 is identical with that derived from mechanism III and with the empirical form (eq 10) suggested by Sykes.[9] Using the parameters, *a*, *b*, and *c*,[9] the following constants (25°) are calculated: $k_3 = 3.35 \times 10^2\ M^{-1}\ \text{sec}^{-1}$, $k_2/k_4 = 1.1 \times 10^{-2}\ M$, $k_{-3}/k_4 = 0.15\ M$, and $k_2/k_{-3} = 0.073$.

Mechanism IV features two activated complexes ($[\text{V(OH)Cr}^{4+}]^*$) of equal composition. They differ in the species from which they are formed (reactants or intermediate) and the species into which they decompose (intermediate or products).[12]

Mechanism IV appears to be reasonable. The kinetic importance of the species VOH^{2+} conforms to current notions about the relative reactivities of hydrolyzed and unhydrolyzed aquo ions in electron-transfer reactions proceeding *via* bridged mechanisms.[13] Furthermore, the decomposition of the binuclear intermediate V(OH)Cr^{4+} by parallel acid-independent (eq 3) and acid-dependent (eq 8) paths is in agreement with findings in related systems.[14]

In the mechanisms discussed above, the reaction of vanadium(III) (hydrolyzed or unhydrolyzed) with chromium(II) results in the formation of the binuclear intermediate V(OH)Cr^{4+}. Two additional mechanisms,[15,16] also consistent with eq 10, feature a reaction between VOH^{2+} and Cr^{2+} that yields products directly.

Mechanism V

$$\text{V}^{3+} + \text{Cr}^{2+} + \text{H}_2\text{O} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \text{V(OH)Cr}^{4+} + \text{H}^+ \qquad (2)$$

$$\text{V(OH)Cr}^{4+} \xrightarrow{k_2} \text{V}^{2+} + \text{CrOH}^{2+} \qquad (3)$$

$$\text{VOH}^{2+} + \text{Cr}^{2+} \xrightarrow{k_5} \text{V}^{2+} + \text{CrOH}^{2+} \qquad (13)$$

This mechanism leads to the rate law

$$\text{rate} = \frac{(k_1k_2 + k_{-1}k_5Q) + k_2k_5Q[\text{H}^+]^{-1}}{k_2 + k_{-1}[\text{H}^+]}[\text{V}^{3+}][\text{Cr}^{2+}] \qquad (14)$$

The values $k_1 = 3.9\ M^{-1}\ \text{sec}^{-1}$, $k_5 = 22.8\ M^{-1}\ \text{sec}^{-1}$, and $k_2/k_{-1} = 0.16\ M$ are computed from the empirical parameters given by Sykes.[9]

Mechanism VI

$$\text{VOH}^{2+} + \text{Cr}^{2+} \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} \text{V(OH)Cr}^{4+} \qquad (7)$$

$$\text{V(OH)Cr}^{4+} + \text{H}^+ \xrightarrow{k_4} \text{V}^{2+} + \text{Cr}^{3+} + \text{H}_2\text{O} \qquad (8)$$

$$\text{VOH}^{2+} + \text{Cr}^{2+} \xrightarrow{k_5} \text{V}^{2+} + \text{CrOH}^{2+} \qquad (13)$$

This mechanism yields the rate law

$$\text{rate} = \frac{(k_3 + k_5)k_4Q + k_{-3}k_5Q[\text{H}^+]^{-1}}{k_{-3} + k_4[\text{H}^+]}[\text{V}^{3+}][\text{Cr}^{2+}] \qquad (15)$$

where $k_3 = 3.12 \times 10^2\ M^{-1}\ \text{sec}^{-1}$, $k_5 = 22.8\ M^{-1}\ \text{sec}^{-1}$, and $k_{-3}/k_4 = 0.16\ M$.

The mechanistic ambiguity in the interpretation of the rate law represented by eq 10 arises because, although the form of the rate law defines the composition of the activated complexes, the rate law does not specify[6,12] (a) the order of formation of the activated complexes, (b) the species (reactants or intermediates) which generate the activated complexes, and (c) the decomposition products (intermediates or products) of the activated complexes.

Recently, Espenson[17] indicated that there is no requirement, in the available[8] kinetic data, for the three-parameter rate law (eq 10) proposed by Sykes.[9] However, whether eq 1 or 10 provides a better fit of the experimental data, we are still faced with the problem of alternate mechanisms consistent with either rate law.

A mechanistic ambiguity related to the sequence of formation of activated complexes arises in the case of the plutonium(VI)–uranium(IV) reaction.[18] The proposed scheme

$$\text{U}^{4+} + \text{PuO}_2^{2+} + 2\text{H}_2\text{O} \underset{k_{-1}'}{\overset{k_1'}{\rightleftharpoons}} \text{int} + (p + q)\text{H}^+ \qquad (16)$$

$$\text{forward rate} = k_1'[\text{U}^{4+}][\text{PuO}_2^{2+}][\text{H}^+]^{-p} \qquad (17)$$

$$\text{reverse rate} = k_{-1}'[\text{int}][\text{H}^+]^q \qquad (18)$$

$$\text{int} \xrightarrow{k_2'} \text{PuO}_2^+ + (r + s)\text{H}^+ \qquad (19)$$

$$\text{rate} = k_2'[\text{int}][\text{H}^+]^{-r} \qquad (20)$$

leads to the equation (after correcting for the hydrolysis of U^{4+})

$$\frac{1}{k'([\text{H}^+] + K)} = \frac{[\text{H}^+]^{p-1}}{2k_1'} + \frac{k_{-1}'}{2k_1'k_2'}(\text{H}^+)^{p+q+r-1} \qquad (21)$$

From the observation that a plot of $1/k'([\text{H}^+] + K)$ *vs.* $[\text{H}^+]$ is linear, Newton[18] concluded that $p - 1 = 0$ and $p + q + r - 1 = 1$. The mechanism represented by eq 16–21 is entirely analogous to mechanism I when $p = q = 1$ and $r = 0$. It must be noted, however, that the linearity of the plot of $1/k'([\text{H}^+] + K)$ *vs.* $[\text{H}^+]$ indicates that one of the terms on the right-hand side of eq 21 is independent of $[\text{H}^+]$, while the other is first order in $[\text{H}^+]$. Newton[18] assumed that $p - 1 = 0$ and $p + q + r - 1 = 1$. The alternate choice $p - 1 = 1$ and $p + q + r - 1 = 0$ appears to be reasonable and leads to a mechanism entirely analogous to mechanism II when $p = 2$, $q = 0$, and $r = -1$.

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[13] A. Zwickel and H. Taube, *Discussions Faraday Soc.*, **29**, 73 (1960).

[14] T. W. Newton and F. B. Baker, *Inorg. Chem.*, **3**, 569 (1964); T. J. Conocchioli, E. J. Hamilton, Jr., and N. Sutin, *J. Am. Chem. Soc.*, **87**, 926 (1965); J. H. Espenson, *Inorg. Chem.*, **4**, 1533 (1965).

[15] The author is indebted to Dr. T. W. Newton for suggesting these mechanisms.

[16] Mechanisms III to VI can be derived readily using the electrical analogs suggested by Newton.[6]

[17] J. H. Espenson and D. W. Carlyle, *Inorg. Chem.*, **5**, 586 (1966).

[18] T. W. Newton, *J. Phys. Chem.*, **62**, 943 (1958).

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