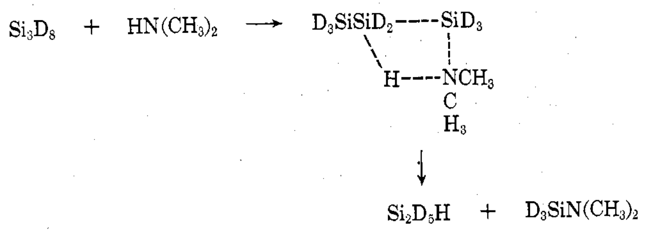
the total pressure of this mixture was very close to that expected without an interaction between SiH_4 and $N(CH_3)_3$.

(2) **Si_2H_6–$N(CH_3)_3$, Si_3H_8–$N(CH_3)_3$.**—The vapor pressures of equimolar mixtures of $N(CH_3)_3$ and either Si_2H_6 or Si_3H_8 were below those calculated by Raoult's law. For Si_2H_6–$N(CH_3)_3$, the vapor pressures were 0.79, 0.71, and 0.57 of that calculated by Raoult's law at −63, −78, and −95°, respectively. For Si_3H_8–$N(CH_3)_3$, the vapor pressures were 0.54 and 0.29 of that calculated by Raoult's law at −63 and −78°, respectively. A Si_3H_8–$N(CH_3)_3$ mixture (0.55 mmol each) was maintained at −78° and allowed to distil into a trap cooled to −196°. After 1 hr only 5% of the mixture remained while after 2 hr nothing remained in the −78° trap.

These data demonstrate that weak complex formation does occur between $N(CH_3)_3$ and Si_2H_6 or Si_3H_8. Further, the data with all three silanes indicate an increase in the interaction between $N(CH_3)_3$ and the silanes in the order $SiH_4 < Si_2H_6 < Si_3H_8$. This order should be a measure of the relative Lewis acidities of the silanes with $N(CH_3)_3$ as the reference base.

(3) **Reaction of Si_3H_8 with $HN(CH_3)_2$.**—The above conclusion is also consistant with the following results. The vapor pressure of a $HN(CH_3)_2$–Si_2H_6 mixture was less than calculated by Raoult's law. While no reaction was observed between $HN(CH_3)_2$ and Si_2H_6, Si_2H_6 (0.44 mmol) was produced from the 1 hr reaction of Si_3H_8 with $HN(CH_3)_2$ at −78°. The other product (0.44 mmol) was $SiH_3N(CH_3)_2$ identified by its infrared,[7] nmr,[8] and mass spectrum. The above experiment was repeated with $HN(CH_3)_2$ and Si_3D_8 yielding Si_2D_5H[9] and $D_3SiN(CH_3)_2$. The infrared spectrum of $D_3SiN(CH_3)_2$ contained only Si–D stretching bands. The results from the reaction with Si_3D_8 suggest the mechanism



In the above mechanism the disilanyl group acts as a halogen.[10] The occurence of this reaction with

$$SiH_3Br + HN(CH_3)_2 \longrightarrow HBr + H_3SiN(CH_3)_2 \qquad (1)$$

Si_3H_8 but not with Si_2H_6 (under the same conditions) can be explained by an increased Lewis acidity of Si_3H_8 compared to Si_2H_6.

Acknowledgment.—The authors are indebted to the Army Research Office for financial support.

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(7) M. J. Butler and D. C. McKean, *Spectrochim. Acta*, **21**, 485 (1965).

(8) E. A. V. Ebsworth and N. Sheppard, *J. Inorg. Nucl. Chem.*, **9**, 95 (1959).

(9) M. A. Ring, G. D. Beverly, F. H. Koester, and R. P. Hollandsworth, *Inorg. Chem.*, **8**, 2033 (1969).

(10) S. Sujishi and S. Witz, *J. Amer. Chem. Soc.*, **76**, 4631 (1954).

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RECEIVED DECEMBER 2, 1971

Acid-Catalyzed Substitution of OH⁻ in the Hydrogen Chromate(VI) Anion by Various Ligands. Free Energy Relationships and Mechanistic Considerations[1]

Sir:

Oxidation–reduction reactions involving the chromium(III)–chromium(VI) couple have been extensively investigated.[2] In many instances, the initial step in the reduction of the hydrogen chromate anion involves the formation of a chromium(VI)–substrate complex. In recent years, mostly through the work of Haight, Beattie, and coworkers, kinetic and thermodynamic information about these chromium(VI)–substrate complexes has become available.[3,4] It is the purpose of this note to point out the existence of a linear free energy relationship between the kinetic and the equilibrium data for the formation and dissociation of the complexes, and to make some comments about the mechanism of substitution at the chromium(VI) center.

All of the reactions under consideration can be represented by eq 1 or 2. A stoichiometric distinction between these two types of reactions is made depending upon whether hydrogen ions are consumed (forward reaction in eq 1) or act as catalytic agents (eq 2). However, there is no kinetic difference between the two classes, the rate law for the forward reactions being given in all cases by eq 3. When the substrate Su is

$$X^{n-} + HCrO_4^- + H^+ \underset{k_r}{\overset{k_f}{\rightleftharpoons}} H_2O + CrO_3X^{n-} \quad Q \qquad (1)$$

$$HX^{n-} + HCrO_4^- + H^+ \underset{k_r'}{\overset{k_f}{\rightleftharpoons}} H_2O + CrO_3X^{(n+1)-} + H^+ \quad Q' \qquad (2)$$

$$\text{rate} = k_f[HCrO_4^-][H^+][Su] \qquad (3)$$

basic, the reported rate law has the form ($HSu^+ = HCrO_4^-, HS_2O_3^-$)[3,5]

$$\text{rate} = k_f'[HCrO^-][HSu^+] \qquad (4)$$

However, using the known ionization constants of the weak acids HSu^+, we have chosen to recast these rate laws in the form of eq 3. In this manner, the reactions of the chromate and thiosulfate ions can be compared directly with the reactions of the remaining substrates.

The available values of k_f, k_r, and Q[6] are presented in Table I. It will be seen that the chromium(VI) center exhibits a strong equilibrium discrimination toward the various substrates (*ca.* 10^7), but only a modest (a factor of 10) kinetic discrimination toward addition of the substrate. These trends are entirely analogous to those observed previously for the anation reactions of aquopentaamminecobalt(III).[7,8] The wide variation

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[1] This work was supported in part by Grant GP-9669 from the National Science Foundation.

[2] For a classic review see F. Westheimer, *Chem. Rev.*, **45**, 419 (1949). For an account of more recent developments, see J. H. Espenson, *Accounts Chem. Res.*, **3**, 347 (1970).

[3] K. A. Muirhead, G. P. Haight, Jr., and J. K. Beattie, *J. Amer. Chem. Soc.*, **94**, 3006 (1972).

[4] C. Lin and J. K. Beattie, *ibid.*, **94**, 3011 (1972).

[5] J. H. Swinehart and G. W. Castellan, *Inorg. Chem.*, **3**, 278 (1964).

[6] Unless the equilibrium quotient Q was determined independently, the values of Q are k_f/k_r.

[7] C. H. Langford, *Inorg. Chem.*, **4**, 265 (1965).

[8] A. Haim, *ibid.*, **9**, 426 (1970).

TABLE I

KINETIC AND EQUILIBRIUM DATA FOR REACTIONS 1 AND 2 (25°, VARIABLE (0.10–3.0 M) IONIC STRENGTH)

Reaction	k_f[a]	k_r[b]	Q[c]	Ref
$H^+ + H_2PO_4^- + HCrO_4^- \rightleftharpoons HO_3POCrO_3^{2-} + H_2O + H^+$	1.2×10^5	2.0×10^4	6	*d*
$H^+ + H_2PO_3^- + HCrO_4^- \rightleftharpoons HO_2POCrO_3^{2-} + H_2O + H^+$	5×10^5	6.0×10^4	8	*e*
$H^+ + HCrO_4^- + HCrO_4^- \rightleftharpoons O_3CrOCrO_3^{2-} + H_2O + H^+$	6.2×10^5	6.3×10^3	98	*f*
$H^+ + NCS^- + HCrO_4^- \rightleftharpoons (NCS)CrO_3^- + H_2O$	5.4×10^5	2.4×10^3	220	*g*
$H^+ + S_2O_3^{2-} + HCrO_4^- \rightleftharpoons (S_2O_3)CrO_3^{2-} + H_2O$	3.7×10^5	2.1	2.2×10^5 [h]	*i*
$H^+ + CrO_4^{2-} + HCrO_4^- \rightleftharpoons O_3CrOCrO_3^{2-} + H_2O$	9×10^5 [j]	2.7×10^{-2}	3.3×10^7	*k*

[a] Units are M^{-2} sec^{-1}. [b] Units are sec^{-1} or M^{-1} sec^{-1} depending on whether the stoichiometric equation is given by reaction 1 or 2, respectively. [c] Units are M^{-2} or M^{-1}. See footnote *b*. [d] S. A. Frenesson, J. K. Beattie, and G. P. Haight, *J. Amer. Chem. Soc.*, **90,** 6018 (1968). [e] S. A. Frenesson, J. K. Beattie, and G. P. Haight, *Acta Chem. Scand.*, **23,** 3277 (1969). [f] J. Pladziewicz and J. H. Espenson, *Inorg. Chem.*, **10,** 634 (1971). [g] Reference 4. [h] Calculated as $1.2 \times 10^4/5.4 \times 10^{-2}$, where 1.2×10^4 is Q for $HS_2O_3^- + HCrO_4^- \rightleftharpoons (S_2O_3)CrO_3^{2-} + H_2O$, and 5.4×10^{-2} is the acid dissociation constant of $HS_2O_3^-$. [i] Reference 3. [j] Calculated as $1.8/2(1.0 \times 10^{-6})$, where 1.8 is the measured second-order rate constant for $2HCrO_4^- \rightarrow Cr_2O_7^{2-} + H_2O$, 1.0×10^{-6} is the acid dissociation constant of $HCrO_4^-$, and 2 is a statistical correction that makes the symmetrical dimerization reaction comparable to the unsymmetrical condensation reactions. [k] Reference 5.

in equilibrium constants, contrasted with the insensitivity of the rate constants to the identity of the incoming ligand, suggests, at most, a very weak bond between chromium(VI) and the ligand in the transition state. This qualitative conclusion, which was previously pointed out,[3] is depicted quantitatively in Figure 1 where a log k_r *vs.* $-\log Q$ plot has been constructed.[9] Assuming a linear relationship, the calculated (least squares) slope is 0.94. Since a linear free energy correlation with slope 1.0 between $\Delta G^{\ddagger}$ and ΔG° indicates that the transition state closely resembles the products,[10] we conclude that the substrate is, at most, weakly bound to the chromium(VI) center in the transition state.[7,8]

There are at least two mechanisms that incorporate the feature of weak chromium(VI)–incoming ligand bonding in the transition state. In the rate-determining proton-transfer mechanism[4] (mechanism A) the mechanistic sequence consists of three steps: (a) formation of a substrate–chromium complex

$$X + CrO_3OH^- \underset{k_{-0}}{\overset{k_0}{\rightleftharpoons}} XCrO_3OH^- \qquad (5)$$

(b) proton transfer to the OH bound to the Cr(VI) center in the substrate–chromium complex

$$XCrO_3OH^- + H^+ \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} XCrO_3OH_2 \qquad (6)$$

(c) loss of water from the pentacoordinate chromium(VI) intermediate

$$XCrO_3OH_2 \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} XCrO_3 + H_2O \qquad (7)$$

This is essentially a limiting associative mechanism in which the loss of the leaving group from the intermediate of increased coordination number is accomplished following the addition of a proton. In order to account for the third-order rate law and for the insensitivity of the rate constant k_f to the nature of the incoming ligand, it was postulated[4] that the formation of the Cr(VI)–substrate complex is kinetically diffusion-controlled and thermodynamically weak, and that the proton addition in eq 6 also proceeds with a diffusion-controlled rate constant of 10^{10} M^{-1} sec^{-1}. Finally, it was assumed that the pentacoordinate intermediate $XCrO_3OH_2$ loses water faster than a proton. On the basis of this mechanism

$$k_f = \frac{k_0}{k_{-0}} k_1$$

and

$$k_r = \frac{k_{-2}}{k_2} k_{-1}$$

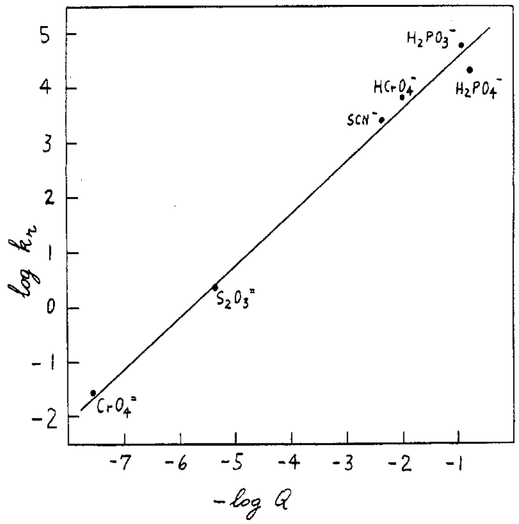

Figure 1.—Plot of log k_r *vs.* $-\log Q$ for the reactions in Table I. The solid line is defined by the least-squares equation $\log k_r = 5.47 + 0.94 \log Q$.

An alternative and kinetically indistinguishable mechanism (mechanism B), previously postulated to explain the formation of CrO_5 from $HCrO_4^-$ and H_2O_2,[11] consists of two steps: (a) diffusion-controlled protonation

$$CrO_3OH^- + H^+ \rightleftharpoons CrO_3OH_2 \quad Q_8 \qquad (8)$$

(b) rate-determining substitution of the coordinated water by the incoming ligand

$$CrO_3OH_2 + X \underset{k_{-9}}{\overset{k_9}{\rightleftharpoons}} CrO_3X + H_2O \qquad (9)$$

On the basis of this mechanism, $k_f = Q_8 k_9$ and $k_r = k_{-9}$. In order to account for the independence of k_f

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[9] It would appear at first glance that, since some of the rate constants k_r are first order whereas others are second order, a plot constructed using the two types of rate constants cannot yield consistent results. However, on further examination it is recognized that if for the reactions

$$HX + CrO_3OH^- + H^+ \underset{k_r}{\overset{k_f}{\rightleftharpoons}} CrO_3XH + H_2O$$

a plot of log k_r *vs.* $-\log Q$ is linear with slope 1.0 and intercept log k_f, then for the reactions

$$HX + CrO_3OH^- + H^+ \underset{k_r'}{\overset{k_f}{\rightleftharpoons}} CrO_3X^- + H_2O + H^+$$

a plot of log k_r' *vs.* $-\log Q'$ (where $Q' = Q \times Qi$ and Qi is the ionization constant for the reaction $CrO_3XH \rightleftharpoons CrO_3X^- + H^+$) also will have a slope 1.0 and an intercept log k_f.

[10] J. E. Leffler and E. Grunwald, "Rates and Equilibria of Organic Reactions," Wiley, New York, N. Y., 1963.

[11] M. Orhanovic and R. G. Wilkins, *J. Amer. Chem. Soc.*, **89,** 267 (1967).

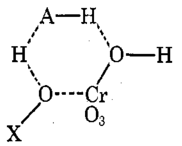
with respect to the nature of the incoming ligand, it is necessary to postulate that bond breaking is the most important feature of the activation process for eq 9, and therefore the reaction sequence is viewed as a dissociative mechanism in which the departure of the leaving group is facilitated by protonation.

To be sure, it is not possible to distinguish between the two mechanisms on the basis of the rate law, and this represents another example of ambiguities in mechanistic interpretations.[12] In the present case, the mechanistic ambiguity is ascribed to our inability to establish the order of aggregation of the three species required to define the composition of the activated complex for the reaction. However, for the particular system under scrutiny, it is possible to rule out the rate-determining proton transfer mechanism on the basis of phenomenological considerations related to diffusion-controlled reactions.[13] According to mechanism A, $k_f = k_0k_1/k_{-0}$. Since k_0 and k_1 are rate constants for diffusion-controlled processes ($\sim 10^{10}\ M^{-1}\ \text{sec}^{-1}$) and k_f is of the order of $5 \times 10^5\ M^{-2}\ \text{sec}^{-1}$, we calculate a value for k_{-0} of $\sim 2 \times 10^{14}\ \text{sec}^{-1}$, and therefore a lifetime of $\sim 5 \times 10^{-15}$ sec for the complex $XCrO_3OH^-$. Even allowing for a possible electrostatic repulsion between X and CrO_3OH^-, such a lifetime is approximately 4 orders of magnitude smaller than the lifetime of an encounter complex.[14] Consequently, the proposed[4] assignment of rate constants is rejected because it predicts a physically impossible value for k_{-0}.

Mechanism A can be modified, still retaining the feature of rate-determining proton transfer to $XCrO_3OH^-$, by decreasing the rate constant for the formation of the pentacoordinate species in eq 5 in order to obtain a physically permissible value for k_{-0}. Using $k_1 = 10^{10}\ M^{-1}\ \text{sec}^{-1}$ and $k_{-0} < 10^{11}\ \text{sec}^{-1}$, we calculate a value of $k_0 < 5 \times 10^4\ M^{-1}\ \text{sec}^{-1}$. However, even in this modified form, the mechanism does not seem satisfactory. The observed rate constant k_f has a contribution of the equilibrium constant k_0/k_{-0} for the *nucleophilic addition* of the incoming ligand to the Cr(VI) center to produce the pentacoordinate intermediate $XCrO_3OH^-$. With a tetracoordinate Cr(VI) center that covers a range of almost 10^7 in its thermodynamic affinity toward various nucleophiles, it does not seem reasonable that the corresponding pentacoordinate Cr(VI) center would not display some discrimination for the nucleophiles. On the basis of these considerations, we tend to discount mechanism A.

An alternate assignment of rate constants in mechanism A is $k_f = k_0k_1k_2/k_{-0}k_{-1}$ and $k_r = k_{-2}$. In this interpretation, the pentacoordinate intermediate $XCrO_3OH_2$ is in rapid equilibrium with H^+, X^-, and CrO_3OH^-, and loss of water from the intermediate is rate-determining. Again, the equilibrium constant k_0/k_{-0} for the nucleophilic addition of X^- to the Cr(VI) center is included in the observed rate constant k_f, and therefore the argument advanced against the first modification of mechanism A is still valid.

The dissociative mechanism B accounts nicely for the specific acid catalysis, but leaves unanswered the question of the general acid catalysis observed for $H_2PO_4^-$,[15] $H_2PO_3^-$,[16] and $HCrO_4^-$.[17] However, it must be noted that although general acid catalysis requires a rate-determining proton transfer for the path catalyzed by a general acid, the corresponding hydrogen ion catalyzed path need not be limited by proton transfer. An attractive pathway to account for the general acid catalysis involves a concerted mechanism whereby loss of OH^- from CrO_3OH^- and loss of H^+ from XOH^- ($X = PO_3H$, PO_2H, CrO_3) are assisted by the general acid HA by means of the cyclic transition state[17]



X = PO_3H, PO_2H, CrO_3
HA = general acid

Finally, it is noteworthy that the kinetic and free energy relationships observed in the Cr(VI) system are exactly parallel in the N(III) system[18] (X is a halide or thiocyanate)

$$HNO_2 + H^+ + X^- \underset{k_r}{\overset{k_f}{\rightleftharpoons}} H_2O + XNO \qquad (10)$$

The rate low for the formation of XNO is given by $k_f[H^+][HNO_2][X^-]$. Moreover, the equilibrium constants for formation of ClNO and NCSNO differ by a factor of *ca.* 10^5, whereas the corresponding values of k_f differ by less than a factor of two. The mechanism proposed[18] to account for the substitution reactions on N(III) is given by eq 11 and 12. With the proviso that

$$ONOH + H^+ \rightleftharpoons ONOH_2^+ \text{ Rapid} \qquad (11)$$

$$X^- + ONOH_2^+ \rightleftharpoons XNO + H_2O \text{ Rate determining} \qquad (12)$$

bond breaking is the most important feature of the activation process in reaction 12, this mechanism is identical with the one proposed above to account for the observations on the substitution reactions of $HCrO_4^-$.

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[12] A. Haim, *Inorg. Chem.*, **5**, 2081 (1966).

[13] I. Amdur and G. G. Hammes, "Chemical Kinetics," McGraw-Hill, New York, N. Y., 1966, p 59.

[14] S. W. Benson, "The Foundations of Chemical Kinetics," McGraw-Hill, New York, N. Y., 1960, p 496.

[15] S. A. Frenesson, J. K. Beattie, and G. P. Haight, *J. Amer. Chem. Soc.*, **90**, 6018 (1968).

[16] S. A. Frenesson, J. K. Beattie, and G. P. Haight, *Acta Chem. Scand.*, **23**, 3277 (1969).

[17] R. Baharad, B. Perlmutter-Hayman, and M. A. Wolff, *J. Phys. Chem.*, **73**, 4391 (1969).

[18] D. E. Klimek, B. Grossman, and A. Haim, *Inorg. Chem.*, in press.

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RECEIVED JUNE 12, 1972

Conformations of Six-Membered Rings in Tris Metal Complexes. A Skew-Boat Conformation in $[Cr(NH_2CH_2CH_2CH_2NH_2)_3]^{3+}$

Sir:

The conformational problem presented by complexes containing six-membered chelate rings is similar to that posed by cyclohexane. For the ring system