constants, k_{-1}, for pyridine were calculated from the equilibrium constants. Table II lists the calculated rate constants, k_1 and k_{-1}, for the pyridine and thiocyanate reactions at various temperatures.

TABLE II

RATE CONSTANTS FOR THE LIGAND SUBSTITUTION REACTIONS IN WATER[a]

$$CH_3Co(DH)_2OH_2 + L \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} CH_3Co(DH)_2L$$

L = py			L⁻ = NCS⁻ [b]		
Temp, °C	$10^{-1}k_1$, M^{-1} sec⁻¹	10^2k_{-1},[c] sec⁻¹	Temp, °C	$10^{-1}k_1$, M^{-1} sec⁻¹	k_{-1}, sec⁻¹
10	2.99[d]				
11	1.2	0.47	10	4.96[d]	
15	2.0	0.88	15	5.2	0.70
19	3.2	1.6	20	8.9	1.3
25	6.8	4.1	25	15	2.6
31	12	8.7	30	26	4.3
34	21	17	35	43	7.3
47	88	98	40	63	14

[a] The concentration of $CH_3Co(DH)_2OH_2$ in these experiments was 2.0×10^{-4} to 5.0×10^{-4} M. The concentration of ligand was 50–100 times that of the $CH_3Co(DH)_2OH_2$ concentration. [b] Kinetic data for NCS^- substitution were estimated from plots of k_{obsd} *vs.* $[NCS^-]$. [c] Obtained from $k_{-1} = k_1/K_f$. [d] Data of Crumbliss and Wilmarth[1] at unit ionic strength added for comparison.

TABLE III

ACTIVATION PARAMETERS FOR THE SUBSTITUTION REACTION[a]

$$CH_3Co(DH)_2OH_2 + L \rightleftarrows CH_3Co(DH)_2L$$

Ligand	ΔH^*, kcal mol⁻¹	ΔS^*, eu
Pyridine	20.5 ± 0.4	19 ± 1.5
NCS^-	17.5 ± 0.4	10 ± 1.5

[a] ΔH^* and ΔS^* were obtained from the slope and intercept, respectively, of a plot of log k_1/T *vs.* $1/T$.

The activation parameters listed in Table III are low for most substitution reactions on cobalt(III) complexes[10] and even low for bis(dimethylglyoximato)-cobalt(III) complexes.[3] Hague and Halpern[3] found $\Delta H^* = 19.1 \pm 1.2$ kcal mol^{-1} and $\Delta S^* = -9 \pm 4$ eu for the reaction of thiocyanate ion with nitro(aquo)bis(dimethylglyoximato)cobalt(III). In contrast to these results the entropy of activation for methyl(aquo)bis(dimethylglyoximato)cobalt(III) is positive instead of negative and this factor contributes more to the rate enhancement than the decrease in the enthalpy of activation by the trans effect of the methyl group. Tobe[11] has proposed that a relatively low entropy of activation in a unimolecular reaction may represent a square-pyramidal transition state and a relatively high entropy of activation a trigonal-bipyramidal transition state. This could apply here if the mechanism is dissociative. However, if the process for these reactions is of the dissociative interchange mechanism (Id) as has been argued,[1,12] then the positive entropy of activation probably merely represents a more flexible transition state in which the dimethylglyoxime ligands are less rigidly held in a plane than that for the nitro(aquo)-bis(dimethylglyoximato)cobalt(III).

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Correspondence

Rate Constants and Activation Parameters for the Formation of Monosubstituted Chromium(III) Complexes

Sir:

The recent compilation of CrX^{2+} formation rate constants[1] prompts us to communicate the results of related calculations made on the same reaction series. The present data supplement those of Espenson[1] in that activation parameters in addition to rate constants are reported. Also considered is the competition between complex formation and the $CrOH_2^{3+}$ water-exchange reaction.

Activation parameters for the reactions of eq 1 and 2 were obtained from aquation activation enthalpies and entropies and the appropriate thermodynamic data.[2-17]

$$CrOH_2^{3+} + X^- \xrightarrow{k} CrX^{2+} + H_2O \qquad (1)$$

$$CrOH^{2+} + X^- \xrightarrow{k_{OH}} Cr(OH)X^+ \qquad (2)$$

$$H^+ + Cr(OH)X^+ \xrightarrow{\text{fast}} CrX^{2+} + H_2O$$

Since most of the experimental work had been performed at elevated temperatures, formation rate constants at 25° were usually calculated directly from the tabulated activation parameters.[18]

Consider the ligands NCS^- through I^- in Table I. Espenson[1] has discussed the ligand-dependent nature of these reactions in light of the free energy correlation found by Swaddle and Guastalla[16] for the CrX^{2+} aquation reactions. It was suggested[1] that bond formation plays a role in the anation reactions, albeit one subordinate to the dissociative loss of water. The activation parameters of Table I (NCS^- through I^-) indicate that the ligand reactivity order is controlled by both $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$, although it can be said that the fastest

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TABLE I

RATE CONSTANTS, ACTIVATION PARAMETERS, WATER-EXCHANGE COMPETITION RATIOS, AND EQUILIBRIUM STABILITY CONSTANTS FOR THE FORMATION OF $Cr(H_2O)_5X^{(3-n)+}$ FROM $Cr(H_2O)_6^{3+}$ AND X^{n-} AT 25°[i,j]

X	10^8k, M^{-1} sec^{-1}	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu	k/k_{ex}, M^{-1}	K_{eq}, M^{-1}	Ref
NCS^-	180	25.1[a]	+0.7[a]	0.7	136	6
NO_3^-	73	26.1	+0.9	0.3	9.7×10^{-3}	7, 8
HF	56	24.2[b]	−6	0.22	26	9, 10
HSO_4^-	13[c]	28.2[c]	+4.5[c]	0.05	1.1	3, 4, 5
Cl^-	2.9	30.3	+8.6	0.01	1.1×10^{-1}	2, 10
Br^-	0.9[d]	28.9[d]	+1.5[d]	4×10^{-3}	2.2×10^{-3}	12, 13
SCN^-	0.4	29.6[e]	+2.1[e,f]	2×10^{-3}	4.5×10^{-4}	6, 14, 15
I^-	0.08	30.6[g]	+6.4[g]	3×10^{-4}	1.0×10^{-5}	10, 16
H_2O	250[h] (sec^{-1})	26.1	. . .	. . .	. . .	19
H_3PO_2	2900	20.3	−11.2	16		k
F^-	2000	31	+24	8	2.2×10^4	9, 10, 17
SO_4^{2-}	1100	29.1	+16.3	4.5	13	4, 5

[a] $\mu = 0.08$ M. [b] ΔH corrected using $\Delta C_p \simeq -30$ cal deg^{-1}. [c] Calculated using $K_a^{HSO_4}$ thermodynamic parameters determined at $\mu = 2$ M. [d] Calculated using equilibrium parameters determined at $\mu = 2$ M. [e] Estimated assuming ΔS is the same for $CrSCN^{2+}$ and $CrNCS^{2+}$. [f] Refers to mechanism 3 in ref 15; [g] Calculated using equilibrium parameters determined at 4.2 M. [h] $k_{ex} = 0.693/t_{1/2}$. [i] In most cases the uncertainties in the activation parameters are about ±1 kcal/mol and ±3 eu. [j] Except where noted, the entries have been calculated from kinetic and thermodynamic parameters obtained at $\mu = 0.5$–1 M. [k] J. H. Espenson and D. E. Binau, *Inorg. Chem.*, **9**, 426 (1970).

anations are those with the smallest activation enthalpies. The lowest enthalpies are not too far from the value for the $CrOH_2^{3+}$ water-exchange reaction,[19] and the k/k_{ex} ratios (where k_{ex} is the first-order water-exchange rate constant) are all less than unity. These data point to the importance of water dissociation in the transition state and, together with the ligand dependency, would seem to be consistent with a "ligand-assisted water loss," as proposed by Espenson.[1]

It is interesting that some k/k_{ex} ratios are considerably smaller than the values found in the anation reactions of $Co(NH_3)_5OH_2^{3+}$ [20–22] and numerous bipositive hexaaquo complexes.[22,23] We suggest that the ligand dependence and small k/k_{ex} ratios are in part related to the feeble thermodynamic stability of many CrX^{2+} species (Table I). Ligand assistance is expected in endothermic substitution reactions, since the transition state is likely to resemble the product with respect to ligand–metal bond formation.[24]

Haim[25] has discussed competition ratios for $Co(NH_3)_5OH_2^{3+}$ anation reactions in terms of a formal equilibrium constant $Q^{\ddagger}$, which is a measure of the relative affinity of a transition state metal ion center for H_2O and ligand. If the $CrOH_2^{3+}$ series is treated in this way, we have

$$[CrOH_2^{3+}]^{\ddagger} + X^- \overset{Q^{\ddagger}}{\rightleftharpoons} [CrX^{2+}]^{\ddagger} + H_2O \qquad (3)$$

$$k/k_{ex} = Q^{\ddagger} \qquad (4)$$

The formulas $[CrOH_2^{3+}]^{\ddagger}$ and $[CrX^{2+}]^{\ddagger}$ refer to the transition states for water exchange and ligand interchange

$$CrOH_2^{3+} \rightleftharpoons [CrOH_2^{3+}]^{\ddagger} \qquad (5)$$

$$CrOH_2^{3+}, X^- \rightleftharpoons [CrX^{2+}]^{\ddagger} + H_2O \qquad (6)$$

In this interpretation the wide range of $Q^{\ddagger}$ values means that $[CrOH_2^{3+}]^{\ddagger}$ discriminates markedly between different ligands of the same charge. Where $Q^{\ddagger}$ is much smaller than unity, water has a considerably higher affinity for the transition-state Cr(III) center than the ligand X^-. In terms of an energy level diagram (refer to Figure 1 of ref 25), it follows that the difference in energy between $[CrOH_2^{3+}]^{\ddagger}$ and $[CrX^{2+}]^{\ddagger}$ increases as the ground-state complex CrX^{2+} becomes less stable relative to $CrOH_2^{3+} + X^-$. Again the abnormally small k/k_{ex} values may be thought of as reflecting the feeble thermodynamic stability of the CrX^{2+}.

In striking contrast to these results, most $Q^{\ddagger}$ values in the $Co(NH_3)_5OH_2^{3+}$ substitution reactions are in the range of 0.30–0.38, indicating only weak discrimination between ligands and a rather close balance between water and X^- in their affinity for the activated Co(III) center.[25] When making this comparison, differences in overall stability constants for the two series should be noted ($K_{eq} \gtrsim 1$ M^{-1} for most cobalt pentaammines).[26]

The possibility that SO_4^{2-} and F^- constitute special cases in the $CrOH_2^{3+}$ reactions is suggested by the relatively high rates and large k/k_{ex} values for these ligands.[1] These anations may also be considered anomalous in the sense that the high rates are due to favorable activation entropies rather than low activation enthalpies.

One might argue in the case of sulfate that the substitution mechanism is the same as for the other ligands and that the anomalies are due to charge effects. The abnormally large and positive entropy of $CrSO_4^+$ formation ($\Delta S = 29.8 \pm 0.8$ eu at $\mu = 1$ M[4]) and the stability of the outer-sphere complex $CrOH_2 \cdot SO_4^+$ ($K = 12$ M^{-1} at $\mu = 1$ M and 25°[4]) could be cited as supporting evidence.

In reactions between $CrOH_2^{3+}$ and weakly basic anions such as SO_4^{2-} and F^- the kinetic path of eq 7 must

$$CrOH^{2+} + HX \xrightarrow{k_{OH}} CrX^{2+} + H_2O \qquad (7)$$

be taken into consideration.[1,27] Recasting the SO_4^{2-} rate law in terms of eq 7[1] results in a formation rate constant considerably larger than the estimated upper limit for the $CrOH^{2+}$ water-exchange rate constant and a $\Delta H_{OH}^{\ddagger}$ value considerably smaller than the lowest values found for other ligands (see HSO_4^- entry, Table II). These observations are not easily reconciled with the apparent dissociative nature of the $CrOH^{2+}$ anations.[1] It is also noteworthy that the point ($\Delta H_{OH}^{\ddagger}$, $\Delta S_{OH}^{\ddagger}$) for HSO_4^- deviates significantly from the line of Figure 1. Primarily dissociative loss of water *via* the path of eq 1 then offers the simplest interpretation, although the data would also be consistent with an SN2 attack at sulfur *via* path 7.[1]

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TABLE II

RATE CONSTANTS AND ACTIVATION PARAMETERS FOR THE FORMATION OF $Cr(H_2O)_5X^{(2-n)+}$ FROM $Cr(H_2O)_5OH^{2+}$ AND X^{n-} AT 25°[h,k]

X	10^5k^{OH}, M^{-1} sec^{-1}	$\Delta H_{OH}^{\ddagger}$, kcal/mol	$\Delta S_{OH}^{\ddagger}$, eu	Ref
SO_4^{2-}	39	25.5	+11.4	4, 5
HF^{i}	29	19^{b}	−11	9, 10
NO_3^-	9.0	20	−10	7, 8
NCS^-	4.9	22.8^{a}	-0.6^{a}	6
Cl^-	2.8	26.0	+7.7	2, 10
Br^-	1.7^{d}	22.8^{d}	-3.9^{d}	12, 13
SCN^-	0.5	24.5^{e}	$-0.7^{e,f}$	6, 14, 15
I^-	0.26	27.0^{g}	$+11.0^{g}$	10, 16
$HSO_4^{-\,i}$	627^{c}	14.2^{c}	-21^{c}	3, 4, 5
H_2O	$<10^{j}$ (sec^{-1})	. . .	. . .	19

[a-g] See corresponding letter in Table I. [h] The uncertainties in the activation parameters are approximately ±1.5 kcal/mol and ±5 eu. Each entry carries an uncertainty of ±0.4 kcal/mol and ∼±1.5 eu due to the error in the $CrOH_2^{3+}$ acid dissociation parameters which cancels when considering differences between the $\Delta H_{OH}^{\ddagger}$ or $\Delta S_{OH}^{\ddagger}$. Also note that errors associated with the enthalpies and entropies of complex formation cancel when considering differences between the activation parameters of Tables I and II. [i] The rate parameters were calculated from the data for the unprotonated ligand (Table I) according to eq 7. [j] Estimated from a consideration of the lowest acidity employed in the study of ref 19. [k] See footnote *i*, Table I.

Evidence has been presented indicating that eq 7 is the predominant path in the $CrOH_2^{3+}$–F^- reaction.[1,10] The anation activation parameters lend support to this proposal in that the relatively high rate constant calculated for HF in Table II is associated with a relatively small activation enthalpy (compare to F^- in Table I).

It will be noted that the activation enthalpy for the H_3PO_2 reaction[28] is 6 kcal/mol lower than for water exchange. Substitution in this case probably does not involve Cr–OH_2 bond fission.[1]

The possibility of the $CrOH_2^{3+}$–NO_3^- reaction proceeding by means of CrO–NO_2 bond formation has been discussed.[1,16] The NO_3^- activation enthalpy is rather low for a weakly complexing ligand but not inconsistent with the normal mode of substitution.

Espenson[1] has pointed out that the $CrOH^{2+}$ rate constants are less sensitive to differences in ligand nucleophilicity than the $CrOH_2^{3+}$ rate constants. In comparing these two reaction series it is also worth noting that most $CrOH^{2+}$ rate constants are of the same order of magnitude as the upper limit estimated for the $CrOH^{2+}$ water-exchange rate constant.

As in the $CrOH_2^{3+}$ series, the relatively high SO_4^{2-} rate is due to a favorable activation entropy rather than a low activation enthalpy.

The data of Table II indicate that the ligand dependency in the hydroxo series would be considerably larger if it were not for compensating differences in $\Delta H_{OH}^{\ddagger}$ and $\Delta S_{OH}^{\ddagger}$ (Figure 1). The empirical significance of a linear plot of $\Delta H^{\ddagger}$ *vs.* $\Delta S^{\ddagger}$ is that the slope is the temperature at which all reactions following the relation will occur at the same rate within the precision of the fit.[24,29,30] When passing from below to above the "isokinetic temperature" the reaction series changes from a region of control by $\Delta H^{\ddagger}$ to one of control by $\Delta S^{\ddagger}$, and the order of relative rates undergoes an inversion. Although a linear plot can arise from experimental error, the spreads of 7 kcal/mol and 19 eu in the present case argue for a genuine isokinetic relationship. The slope of the straight line of Figure 1 is 330°K, or 58°C, indicating that the reactivity order can change in the temperature range where these reaction rates have been experimentally determined. The parallel between $\Delta\Delta H_{OH}^{\ddagger}$ and $\Delta\Delta S_{OH}^{\ddagger}$ is probably related to ion solvation.[16,24,31,32]

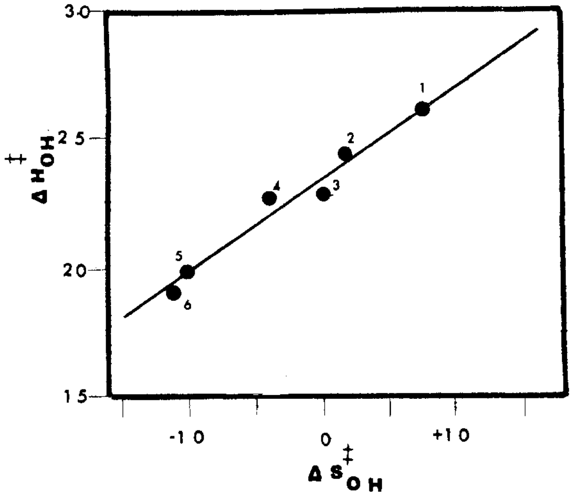

Figure 1.—Compensation between activation enthalpies and entropies in the $CrOH^{2+}$ substitution reactions: (1) Cl^-; (2) SCN^-; (3) NCS^-; (4) Br^-; (5) NO_3^-; (6) HF.

Finally, a comparison of the data of Tables I and II shows that the lability of $CrOH^{2+}$ compared to $CrOH_2^{3+}$ is due mostly to differences in activation enthalpies of *ca.* 4–5 kcal/mol. The lowering of $\Delta H^{\ddagger}$ and the more purely dissociative nature of the $CrOH^{2+}$ reactions may be attributed to stabilization of the transition state by coordinated hydroxide.[1,22]

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LABORATOIRE D'ENZYMOLOGIE
PHYSICOCHIMIQUE ET MOLÉCULAIRE
CENTRE NATIONAL DE LA RECHERCHE
SCIENTIFIQUE FACULTÉ DES SCIENCES
ORSAY, FRANCE

DARWIN THUSIUS

RECEIVED APRIL 10, 1970

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