$$k'' = \frac{k_{\mathrm{HX}}K_{\mathrm{HX}}K_{\mathrm{X}}[\mathrm{H}^+][\mathrm{X}^{n-}](1 + k_{\mathrm{HX}_2}K_{\mathrm{HX}_2}[\mathrm{X}^{n-}]/k_{\mathrm{HX}})}{1 + K_{\mathrm{X}}[\mathrm{X}^{n-}]} \qquad (4)$$

tor are small (which seems likely since $K_{\mathrm{HX}} << 1$). It has been possible to demonstrate the effectiveness of k_{HX_2} and a denominator term $1 + K_{\mathrm{X}}[\mathrm{X}^{n-}]$ for bridge cleavage of the complex $(\mathrm{NH_3})_5\mathrm{Co{-}OH{-}Co(NH_3)_5}^{5+}$,[21] where in this particular case there is a significant contribution from a pathway independent of $[\mathrm{H}^+]$ and $[\mathrm{X}^{n-}]$ which has proved advantageous. If therefore, for $(\mathrm{NH_3})_4\mathrm{Co}\text{-}\mu(\mathrm{NH_2,OH})\text{-}\mathrm{Co(NH_3)_4}^{4+}$, $k_{\mathrm{HX}_2}K_{\mathrm{HX}_2}/k_{\mathrm{HX}} \approx K_{\mathrm{X}}$, then (4) reduces to (5), which is consistent with (2). Thus ion-pair formation may well be effective, even though a less than first-order dependence on $[\mathrm{X}^{n-}]$ is not observed.

$$k'' = k_{\mathrm{HX}}K_{\mathrm{HX}}K_{\mathrm{X}}[\mathrm{H}^+][\mathrm{X}^{n-}] \qquad (5)$$

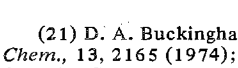
Alternatively, or in some part, the dependence in (2) may be explained in terms of ion pairing of perchlorate as well as uninegative X^- to I. Using this modified approach k may be expressed as in (6), where K_{X} and $K_{\mathrm{ClO_4}}$ are ion-pair formation constants for X^- and $\mathrm{ClO_4}^-$, respectively, and k' is the rate constant for reaction of the X^- ion pair. Perchlorate has often been assumed not to ion pair significantly. However Burnett[22] has recently reinterpreted earlier data for the anation of $[\mathrm{Co(NH_3)_5H_2O}]^{3+}$ by Cl^- and $\mathrm{SO_4}^{2-}$ in terms of many different ion-paired species including perchlorate ion pairs and ion triplets involving both perchlorate and chloride or sulfate. We cannot use such a sophisticated treatment for our studies but it is nevertheless possible to obtain a unified picture by considering perchlorate ion pairing to be as significant as that of any other uninegative ion. With the above assumption rate constants k may be expressed as in (7), and since in our studies $[\mathrm{X}^-] + [\mathrm{ClO_4}^-]$ is always constant at 2.0 M, this reduces to (8). The behavior observed is not inconsistent with (8). Effects of perchlorate are difficult to assess however and verify experimentally at an ionic strength of 2.0 M. The variation in k values and activation parameters for similarly charged species can almost certainly be accounted for by specific ionic effects.

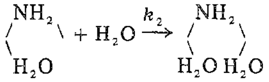
$$k = \frac{k'K_{\mathrm{X}}K_{\mathrm{HX}}}{1 + K_{\mathrm{X}}[\mathrm{X}^-] + K_{\mathrm{ClO_4}}[\mathrm{ClO_4}^-]} \qquad (6)$$

$$k = \frac{k'K_{\mathrm{X}}K_{\mathrm{HX}}}{1 + K_{\mathrm{X}}([\mathrm{X}^-] + [\mathrm{ClO_4}^-])} \qquad (7)$$

$$k = \frac{k'K_{\mathrm{X}}K_{\mathrm{HX}}}{1 + 2K_{\mathrm{X}}} \qquad (8)$$

The case for a limiting SN1 mechanism has also been examined. The reaction sequence may be expressed as in (9)-(11), where k_1 includes the initial protonation equilibrium step. Assuming stationary-state kinetics for the five-coordinate intermediate k may be expressed as in (12). For our data to be consistent with this $(k_{-1} + k_2[\mathrm{H_2O}])$ must be $>> k_3[\mathrm{X}^{n-}]$, and since we know that $k_3[\mathrm{X}^{n-}] \geqslant k_2[\mathrm{H_2O}]$, it follows that $k = k_3K_1$. This leads to a rather unsatisfactory conclusion that $k_{-1} >> k_2[\mathrm{H_2O}]$ and therefore that aquo-bridge closure is much faster than reaction with a water molecule from bulk solvent, and thus coordinated water is a much better nucleophile than an uncoordinated water molecule. This contradiction strongly suggests to the authors that a limiting mechanism is not applicable. The same conclusion is reached when k_{-2} is taken into account, even if this step is rapid compared to k_2.


(9)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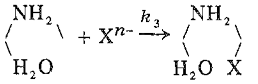
(11)

$$k = \frac{k_1k_3}{k_{-1} + k_2[\mathrm{H_2O}] + k_3[\mathrm{X}^{n-}]} \qquad (12)$$

To summarize we consider the data in the table to be consistent with an SN1 mechanism. The similarity in enthalpies of activation (12.8 ± 0.8 kcal mol^{-1}) for hydroxo-bridge cleavage reactions of singly, doubly, and triply bridged dicobalt(III) complexes[23,24] moreover suggests that a similar mechanism may apply in all these cases.

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Application of the Hammett Equation in Octahedral Aquation of Cobalt(III)-Amine Complexes

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Sir:

In the course of our study[1-4] of cis and trans effects in the acid hydrolysis of complexes of the type *trans*-$[\mathrm{CoLACl}]^{n+}$, where L = $(\mathrm{NH_3})_4$, $(\mathrm{en})_2$ (bis(ethylenediamine)), cyclam (1,4,8,11-tetraazacyclotetradecane, structure **1**), or teta (*meso*-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane, structure **2**) and A = Cl^-, $\mathrm{NO_2}^-$, NCS^-, CN^-, $\mathrm{N_3}^-$, or $\mathrm{NH_3}$, several interesting and significant phenomena were observed. In particular, it was found that the Hammett treatment[5,6] of these kinetic data was most helpful in the understanding of the nature of these reactions.

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(4) W. K. Chau, W. K. Lee, and C. K. Poon, *J. Chem. Soc., Dalton Trans.*, in press.

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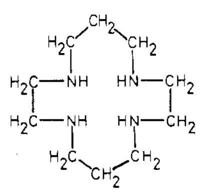
(6) L. P. Hammett, "Physical Organic Chemistry," 2nd ed, McGraw-Hill, New York, N. Y., 1970, p 355.



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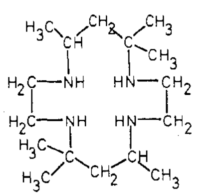

2

Table I. Kinetic Trans Influence for the Acid Hydrolysis of Complexes of the Type *trans*-$[CoLACl]^{n+}$ at 25.0°

	$\log (k_A/k_{Cl})_L$[a]			
A	L = cyclam (σ_A)[b]	L = teta	L = $(en)_2$	L = $(NH_3)_4$
OH^-	4.04		1.66	
NO_2^-	1.59	1.64	1.45	1.18
N_3^-	0.52	0.84	0.87	0.31
Cl^-	0.00	0.00	0.00	0.00
CN^-	−0.36	−0.43	0.37	−0.26
NH_3	−1.18		−2.11	−3.02
NCS^-	−3.00[c]	−3.12	−2.88	−2.70

[a] k_A and k_{Cl} represent the first-order aquation rate constant of *trans*-$[CoLACl]^{n+}$ and *trans*-$[CoLCl_2]^+$, respectively, at 25.0° for a particular L denoted in the subscript of $\log (k_A/k_{Cl})_L$. Data for these rate constants are quoted from (i) C. K. Poon, *Coord. Chem. Rev.*, **10**, 1 (1973), and references therein; (ii) C. K. Poon and H. W. Tong, *J. Chem. Soc., Dalton Trans.*, 1 (1974); and (iii) W. K. Chau, W. K. Lee, and C. K. Poon, *ibid.*, in press. [b] By definition, $\sigma_A = \log (k_A/k_{Cl})_{cyclam}$. [c] The rate constant of *trans*-$[Co(cyclam)NCSCl]^+$ at 25.0° obtained by extrapolation by K. S. Mok, C. K. Poon, and H. W. Tong, *J. Chem. Soc., Dalton Trans.*, 1701 (1972), was found to be in error and the revised rate constant reported in ref *a*(iii) above was used.

Following Hammett's terminology,[5,6] let us take the acid hydrolysis of the series of cyclam complexes as a reference and characterize the orienting effect of A by σ_A which is defined by the equation

$$\sigma_A = \log (k_A/k_{Cl})_{cyclam}$$

in which k_A and k_{Cl} are the first-order aquation rate constants of *trans*-$[Co(cyclam)ACl]^{n+}$ and *trans*-$[Co(cyclam)Cl_2]^+$, respectively, at 25.0°. A series of these constants corresponding to an extensive series of A is collected in Table I. In the same table, corresponding values of $\log (k_A/k_{Cl})_L$ for other series of *trans*-$[CoLACl]^{n+}$ are also included. As shown in Figures 1-3, the plots of $\log (k_A/k_{Cl})_L$ *vs.* σ_A for these four series of complexes are linear over 5 logarithmic units according to the Hammett equation

$$\log (k_A/k_{Cl})_L = \rho_L \sigma_A$$

Here, the reaction constant ρ_L, which is independent of the nature of A, is a measure of the sensitivity of acid hydrolysis of the particular series of *trans*-$[CoLACl]^{n+}$ relative to that of *trans*-$[Co(cyclam)ACl]^{n+}$ to changes in the nature of A [$\rho_{teta} = 1.0$, $\rho_{cyclam} = 1.0$ (by definition), $\rho_{(en)_2} = 0.95$, $\rho_{(NH_3)_4} = 0.85$]. In these plots, some points are lying off the best straight lines. However, this deviation is very significant for these few points and it will be discussed later in the text.

Since teta is different from cyclam in having six methyl substituents in the macrocycle causing serious steric effects at the axial reaction site,[7] the observation that the acid hydrolysis of this series of complexes responds in exactly the same manner both qualitatively and quantitatively as that of the cyclam series to changes in the nature of A of different electronic displacement properties confirms a dissociative mechanism for these reactions; otherwise, the two reaction points for electron-withdrawing orienting ligands (*i.e.,*

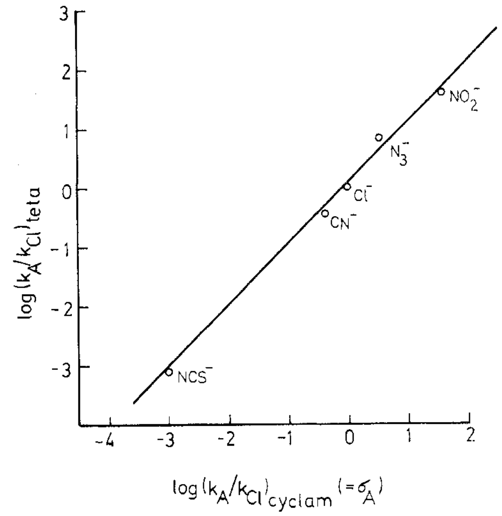

Figure 1. Hammett relationship for the acid hydrolysis of complexes of the type *trans*-$[CoLACl]^{n+}$ at 25.0°. The plot of $\log (k_A/k_{Cl})_{teta}$ *vs.* σ_A.

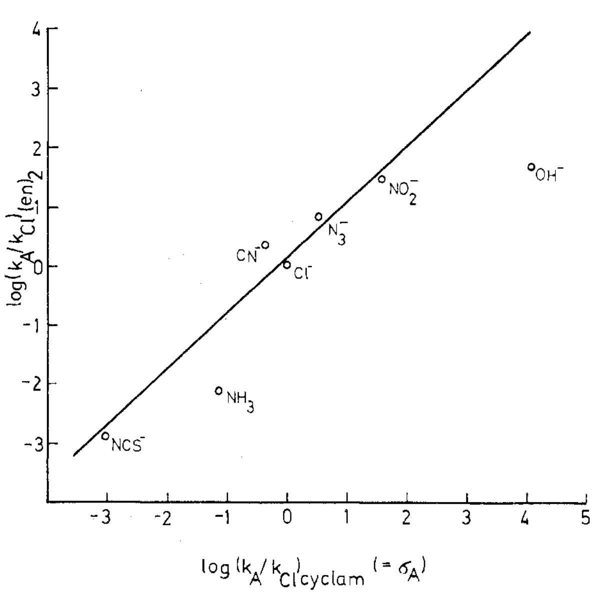

Figure 2. Plot of $\log (k_A/k_{Cl})_{(en)_2}$ *vs.* σ_A.

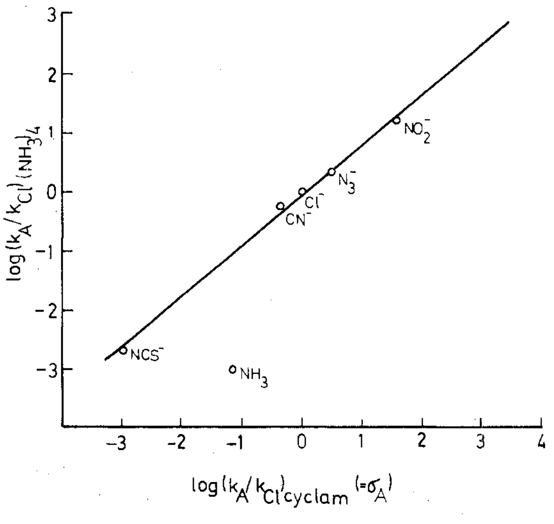

Figure 3. Plot of $\log (k_A/k_{Cl})_{(NH_3)_4}$ *vs.* σ_A.

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(7) W. K. Chau and C. K. Poon, *J. Chem. Soc. A*, 3087 (1971).

$A = CN^-$ and NO_2^-), which are capable of promoting a bimolecular mechanism,[8] should have deviated below the straight line. The observation that $\rho_{teta} = 1.0$ also confirms *that the electronic influence of A is unaffected by steric effect and that these two effects contribute independently to affect the lability of these complexes toward ligand substitution reactions.* In the gross manner, the sensitivity of acid hydrolysis to changes in the electronic nature of A is very nearly the same for these four series of saturated amine complexes. On the other hand, if the difference in the ρ_L values, though very small, is real, the observation that $\rho_{teta} = \rho_{cyclam} > \rho_{(en)_2} > \rho_{(NH_3)_4}$ could be explained in terms of the different extent of nephelauxetic influence[9] of L on ρ_L. It has been shown that,[2,9] for corresponding complexes of the type *trans*-$[CoLACl]^{n+}$, the relative preference of negatively charged ligands to neutral ligands of A decreased in the following order of L: teta = cyclam > $(en)_2$ > $(NH_3)_4$. This implies that both teta and cyclam complexes would be most sensitive and $(NH_3)_4$ complexes least sensitive to changes in these negatively charged orienting ligands A. In any case, this effect is very small.

Another way to treat the same set of kinetic data is to choose the reaction of *trans*-$[CoLCl_2]^+$ complexes as reference and characterize the cis influence of L by σ_L which is defined by the equation

$$\sigma_L = \log (k_L/k_{cyclam})_{Cl}$$

in which k_L and k_{cyclam} are the first-order aquation rate constants of *trans*-$[CoLCl_2]^+$ and *trans*-$[Co(cyclam)Cl_2]^+$, respectively, at 25.0°. The plots of $\log (k_L/k_{cyclam})_A$ *vs.* σ_L for a wide range of A (Table II, Figure 4) also obey the following linear Hammett equation over 3 logarithmic units

$$\log (k_L/k_{cyclam})_A = \rho_A\sigma_L$$

It is most significant to observe that for all uninegatively charged orienting ligands A, irrespective of their π character, the reaction constants ρ_A, which are independent of the nature of L, are close to unity, whereas for the neutral orienting ligand NH_3 $\rho_{NH_3} = 0.42$. This observation strongly supports the earlier proposition[2] that *the kinetic trans influence of these ligands depended primarily on the amount of negative charge donated to the central cobalt(III) ion (i.e., σ donation) by these orienting ligands.* Consequently, ligands of the same charge type have the same response to changes of L and ligands of a lower charge type would be less sensitive to such changes. This immediately explains the cause of deviation of the ammine complexes from the straight-line plots in Figures 2 and 3. The wider spread of kinetic data from linearity in the present plot as compared to those in Figures 1-3 is a consequence of the fact that all four cis ligands are changed from one series to the other in the former plot whereas only one trans ligand A is varied in the latter plots. Obviously, it is most desirable to have available more kinetic data, covering a wider range of neutral orienting ligands, to test the above discussion.

The above linear free energy treatment correlates members of a reaction series, which differ in the nonreacting residue but are identical with respect to the leaving group. This, coupled with the complementary observation[10] of a linear free energy relationship established for the acid hydrolysis of $[Co(NH_3)_5X]^{2+}$ over an extensive series of uninegative leaving groups, confirms that *the acid hydrolysis of all octahedral cobalt(III)-amine complexes is dissociative in nature.*

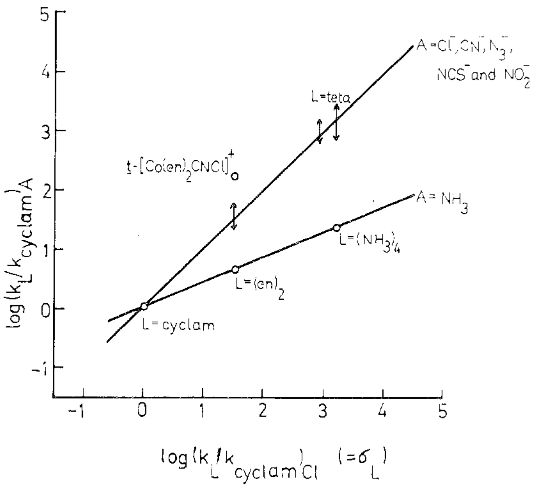

Figure 4. Kinetic cis influence of L on the acid hydrolysis of *trans*-$[CoLACl]^{n+}$ at 25.0°. The plots of $\log (k_L/k_{cyclam})_A$ *vs.* σ_L.

Table II. Kinetic Cis Influence for the Acid Hydrolysis of Complexes of the Type *trans*-$[CoLACl]^{n+}$ at 25.0°

	$\log (k_L/k_{cyclam})_A$[a]					
L	A = Cl (σ_L)[b]	A = NO_2^-	A = N_3^-	A = CN^-	A = NCS^- [c]	A = NH_3
$(NH_3)_4$	3.21	2.80	3.01	3.31	3.51	1.37
teta	2.93	2.98	3.25	2.85	2.81	
$(en)_2$	1.50	1.36	1.86	2.23	1.62	0.67
Cyclam	0.00	0.00	0.00	0.00	0.00	0.00

[a] k_L and k_{cyclam} represent the first-order aquation rate constants of *trans*-$[CoLACl]^{n+}$ and *trans*-$[Co(cyclam)ACl]^{n+}$, respectively, at 25.0° for a particular A denoted in the subscript of $\log (k_L/k_{cyclam})_A$. Data for these rate constants are quoted from references cited in footnote *a* of Table I. [b] By definition, $\sigma_L = \log (k_L/k_{cyclam})_A$. [c] Same as footnote *c* of Table I.

The reason for the deviation of hydroxo complexes from the straight-line plot in Figure 2 is probably due to the special internal conjugate base mechanism[11,12] which speeds up the aquation rate of *trans*-$[Co(cyclam)OHCl]^+$ with respect to that of other members of the cyclam series. On the other hand, the reason behind the deviation of the point with $A = CN^-$ from the straight lines in Figures 2 and 4 is not clear. Judging from the perfect linear plots in Figures 1 and 3, it seems, however, that there is nothing special for CN^- as an orienting ligand, at least, in the acid hydrolysis of $(NH_3)_4$, cyclam, and teta series of complexes.

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