Table II. Kinetics of the *S*-Methyl-*S*-phenylsulfiminium–Iodide Reaction in DMSO–Water Solvents at 20.0° and 0.120 *M* Ionic Strength

$10^2[I^-]_0, M$	$10^2[H^+]_0$, M	$10^4[CH_3$-$(C_6H_5)SN$-$H_2^+]_0, M$		k_I, M^{-2} sec^{-1}
	0.50 Mole Fraction of DMSO			
1.01	7.86	3.73		0.0218
2.10	7.86	3.73		0.0227
			Av	0.022
	0.70 Mole Fraction of DMSO			
0.60	3.93	3.84		0.038
0.60	1.96	3.84		0.035
3.13	0.393	3.84		0.038
5.61	0.393	4.29		0.034
6.04	0.393	3.85		0.032
6.04	0.393	7.7		0.034
6.26	0.393	3.84		0.035
7.00	0.393	2.03		0.036
			Av	0.035
6.03	0.393	3.85		0.032[a]
0.00	0.393	2.03		0[b]
5.61	0.393	4.29		0.034[c]
	1.00 Mole Fraction of DMSO			
5.15	0.314	1.91		0.014

[a] 0.010 *M* KBr added. [b] 0.30 *M* NaBr, λ 265 nm. [c] 0.016 *M* KCl added.

action 1. Substitution takes place at the sulfur center (eq 5). Substitution on nitrogen, which would lead to the same products, can be eliminated by a comparison of the results with those obtained for reactions of $H_2\ddot{N}OSO_3^-$. The hydroxylamine-*O*-sulfonate anion is known to undergo substitution on nitrogen.[5,6] Protonation to give H_3N^+-OSO_3^- does not, in general, lead to an increase in reactivity. In contrast, incorporation of a proton in the activated complex[7-9] is crucial for the reaction of $CH_3(C_6H_5)SNH_2^+$ with iodide. Furthermore, in neutral solution, thiosulfate ion is highly reactive toward $H_2\ddot{N}OSO_3^-$ [6] yet shows no significant reactivity toward $CH_3(C_6H_5)SNH_2^+$ under the same conditions.

The largest k_I values were observed in aqueous solution; in solvents of increasing DMSO content, k_I values decrease, go through a minimum near 0.50 mole fraction of DMSO, and then increase with further increases in DMSO content. The results closely resemble those observed[2] for $(CH_3)_2$-SNH_2^+ in which log k_I paralleled pK_a for the *m*-nitroanilinium ion (an indicator of the proton-donating ability of the solvent mixture) over the entire solvent range. This behavior arises from the importance of equilibrium 4 in determining the rate.

In water at 20°, the ratio of third-order rate constants for reaction of $CH_3(C_6H_5)SNH_2^+$ and of $(CH_3)_2SNH_2^+$, $k_{(CH_3)(C_6H_5)}/k_{(CH_3)_2}$, is 2.6 with iodide and 1.2 with thiourea. Extensive studies have been made of analogous acid-catalyzed reactions of alkyl aryl sulfoxides with halide ions, which proceed *via* substitution at sulfur with an H_2O molecule as the leaving group. The results indicate that the dominant influence of the R group and Ar group is to alter the basicity of the substrate sulfoxide.[9-11] Electron-withdrawing groups decrease the basicity of sulfoxides and, by analogy, $CH_3(C_6H_5)SNH_2^+$ would be expected to react less rapidly than $(CH_3)_2SNH_2^+$, due to a decrease in K_4. The somewhat greater steric requirements of the phenyl group would also lead to a decrease in substitution rate on sulfur. The slightly greater reactivity observed for $CH_3(C_6H_5)SNH_2^+$ suggests that the phenyl group provides a net stabilizing influence on going to the transition state, possibly by delocalization of the increased positive charge that develops on sulfur in the transition state.

Sulfonium sulfur in $CH_3(C_6H_5)SNH_2^+$, with its three bond pairs and one lone pair of electrons, is a predominantly soft electrophilic center as evidenced by the substantial reactivity of iodide (>bromide, chloride) and thiourea.

Acknowledgment. This work was supported by the National Science Foundation under Grant GP-7981.

Registry No. $CH_3(C_6H_5)SNH_2ClO_4$, 51934-47-5; methyl phenyl sulfide, 100-68-5; iodide, 20461-54-5; thiourea, 62-56-6; hydroxylamine-*O*-sulfonic acid, 2950-43-8.

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(5) J. H. Krueger, P. F. Blanchet, A. P. Lee, and B. A. Sudbury, *Inorg. Chem.*, **12**, 2714 (1973).

(6) P. F. Blanchet and J. H. Krueger, *Inorg. Chem.*, **13**, 719 (1974).

(7) Presumably as in eq 4, although the timing of inclusion of the proton is open to question. For analogous reactions of sulfoxides it has been suggested[8,9] that addition of the halide ion nucleophile to form R(Ar)S(X)OH occurs prior to inclusion of the second proton required.

(8) R. A. Strecker and K. K. Andersen, *J. Org. Chem.*, **33**, 2234 (1968).

(9) G. Scorrano, *Accounts Chem. Res.*, **6**, 132 (1973).

(10) For example, $\rho = -0.90$ for HI reduction of para-substituted aryl methyl sulfoxides,[8] but this largely reflects the influence of substitution on the protonation equilibrium $CH_3(Ar)SO + H^+ \rightleftarrows CH_3(Ar)$-$SOH^+$.[11]

(11) Reference 1, p 185.

Correspondence

Mechanism of Hydroxo-Bridge Cleavage in Dicobalt(III) Complexes

AIC401587

Sir:

Octahedral divalent transition metal ions have been shown to undergo substitution by an SN1 process,[1,2] and more recently interest has reverted to reactions of trivalent metal ions. Substantial evidence has been obtained for an SN1 mechanism in the acid hydrolysis of pentaamminecobalt(III) complexes $[Co(NH_3)_5X]^{(3-n)+}$.[3] Varying degrees of associative character have however been proposed for reactions of other trivalent ions, including the d^6 complexes $[Rh(NH_3)_5$-$H_2O]^{3+}$ and $[Ir(NH_3)_5H_2O]^{3+}$,[4] as well as coordinatively unsaturated octahedral complexes with low d-electron populations.[5-7]

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(1) See F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," 2nd ed, Wiley, New York, N. Y., 1967, for a definition of terms SN1 etc. and examples. C. H. Langford and H. B. Gray, "Ligand Substitution Processes," W. A. Benjamin, New York, N. Y., 1965, have introduced alternative terminology.

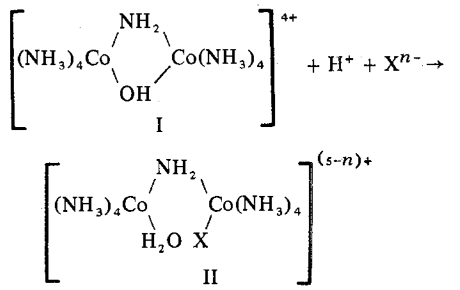
(2) K. Kustin and J. Swinehart, *Progr. Inorg. Chem.*, **13**, 107 (1970).

(3) C. H. Langford, *Inorg. Chem.*, **4**, 265 (1965); A. Haim, *ibid.*, **9**, 429 (1970).

(4) D. Gattegno and F. Monacelli, *Inorg. Chim. Acta*, **7**, 370 (1973), and references therein.

(5) H. Diebler, *Z. Phys. Chem.* (*Frankfurt am Main*), **68**, 64 (1969).

Many trivalent metal ions form binuclear complexes, and the mechanism of substitution giving rise to bridge formation and bridge cleavage is of considerable interest but as yet little investigated. We wish to take this opportunity of summarizing studies on μ-hydroxo cleavage reactions of dicobalt(III)-ammine complexes, in particular those of the μ-amido-μ-hydroxo-bis[tetraamminecobalt(III)] complex $[(NH_3)_4Co\text{-}\mu\text{-}(NH_2,OH)\text{-}Co(NH_3)_4]^{4+}$ (I).[8-15] This work has now reached a stage where generalizations not previously possible can be made. Data obtained for the $[H^+]$-dependent bridge cleavage reactions



(1)

in which formation of II is rate determining are considered. Rate constants, k, as defined in (2) and activation parameters

$$\text{rate} = k[(NH_3)_4Co\text{-}\mu(NH_2,OH)\text{-}Co(NH_3)_4{}^{4+}][H^+][X^{n-}] \quad (2)$$

for 12 different ligand species X^{n-} are listed in Table I. Small contributions from $[H^+]$-independent cleavage processes are sometimes detected[10,11,15] but are not considered further in this note. In all cases the final product is not II but a complex in which the water ligand is replaced by a second X^{n-}, or X^{n-} bridges the two cobalt atoms. The reactions I → II (and beyond) are reversible depending on conditions chosen. Complexes II have not been isolated[16] and at the most there is only small buildup of such species. Their formation is an essential requirement to account for the formation of final products. The reaction sequence is believed to involve protonation of the hydroxo bridge ($K_p < 0.07$ l. mol^{-1} at 25°, $I = 2.0\ M$)[14] in a rapid preequilibrium giving small concentrations of a μ-aquo complex. Subsequently bridge cleavage occurs.

The rate constants in the table fall into three distinct groups depending on the charge on the ligand X^{n-}. Rate constants (10^4k, l.^{2} mol^{-2} sec^{-1}) for the 2− anions are from 130 to 215, for the 1− anions from 1.5 to 11.8, and for the zero-charge reactants from 0.06 to 0.90. An SN2 mechanism can be excluded since rate constants k for $X^{n-} = NCS^-$ and Cl^- give a ratio k_{NCS}/k_{Cl} of 0.5.[11,17] For reactions which have SN2 character the ratio is generally greatly in excess of such values since thiocyanate is a strong nucleophile. Thus ratios k_{NCS}/k_{Cl} for anation reactions of $Cr(H_2O)_6{}^{3+}$ (60),[18] $V(H_2O)_6{}^{3+}$ (>36),[6] and $Mo(H_2O)_6{}^{3+}$ (59)[7] are more in keeping with associative processes. Instead we consider the data obtained to be consistent with an SN1 process.

Table I. Kinetic Parameters for Hydroxo-Bridge Cleavage Reactions of $[(NH_3)_4Co\text{-}\mu(NH_2,OH)\text{-}Co(NH_3)_4]^{4+\,a}$

X^{n-}	$10^4k(25°)$, l.^{2} mol^{-2} sec^{-1}	$\Delta H^{\ddagger}$, kcal mol^{-1}	$\Delta S^{\ddagger}$, cal deg^{-1} mol^{-1}	Ref
$SeO_4{}^{2-}$	130	18.2 ± 0.3	−6.3 ± 0.9	*d*
$SO_4{}^{2-}$	215	17.7 ± 0.05	−6.6 ± 0.15	*e*
$H_2PO_4{}^-$	11.8	19.5 ± 0.7	−6.5 ± 2.3	*f*
$HSeO_4{}^-$	~2			*d*
$HSO_4{}^-$	1.5	17.9 ± 0.25	−16.1 ± 0.8	*e*
Br^-	4.3	17.3 ± 0.8	−16.2 ± 2.6	*g*
Cl^-	9.6	16.2 ± 0.5	−18.1 ± 1.8	*h*
$NO_3{}^-$	4.2^b	13.7 ± 0.6^b	-28.4 ± 2.0^b	*i*
NCS^-	4.8	17.5 ± 0.4	−14.7 ± 1.4	*j*
H_3PO_4	0.85	14.3 ± 0.8	−29.2 ± 2.8	*f*
HOAc	0.065	14.3 ± 0.6	−34.4 ± 1.9	*k*
H_2O	$0.79^{b,c}$	12.5 ± 1.1^b	-35.3 ± 3.6^b	*l*

[a] $I = 2.0\ M$. Rate constants defined as in (2). [b] Determined indirectly. [c] Units: l. mol^{-1} sec^{-1}. [d] Reference 9. [e] Reference 12. [f] Reference 8. [g] Reference 15. [h] Reference 11. [i] Reference 14. [j] S. W. Foong, M. B. Stevenson, and A. G. Sykes, *J. Chem. Soc. A*, 1064 (1970), and unpublished data. [k] Reference 10. [l] Reference 13.

A nonlimiting SN1 process requires ion-pair or outer-sphere complexing (K_o) of X^{n-} to the complex. If k' is the rate constant for the common bridge cleavage process occurring within the ion pair, then $k = k'K_oK_p$. Based on electrostatic models[19] K_o and associated ΔH and ΔS can be estimated[20] and could qualitatively account for the trend in activation parameters. However using this approach K_o is fairly large since the complex has a high charge, and a less than first-order dependence on $[X^{n-}]$ might therefore have been expected. A limiting SN1 mechanism is operative if a five-coordinate intermediate is formed which has a lifetime long enough to enable it to discriminate between nucleophiles in the bulk solution. That is its lifetime is larger than that for exchange processes between the second coordination sphere and the bulk solution. This mechanism should also give a rate law with denominator terms dependent on the concentration of X^{n-} and is therefore not immediately reconcilable with our results.

We consider first the evidence for an SN1 mechanism of the nonlimiting kind. It is possible to obtain an expression in accordance with (2) by considering ion-pair formation between X^{n-} and complex (K_X), protonation of the ion pair (K_{HX}), and formation of a second ion pair with X^{n-} (K_{HX_2}). If then both ion pairs can undergo bridge cleavage, rate constants k_{HX} and k_{HX_2}, respectively, then pseudo-first-order rate constants k'' may be expressed as in (3), which simplifies to (4) assuming that the last two terms in the denomina-

$$k'' = \frac{k_{HX}K_{HX}K_X[H^+][X^{n-}] + k_{HX_2}K_{HX_2}K_{HX}K_X[H^+][X^{n-}]^2}{1 + K_X[X^{n-}] + K_{HX}K_X[H^+][X^{n-}] + K_{HX}K_{HX_2}K_X[H^+][X^{n-}]^2} \quad (3)$$

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(6) R. C. Patel and H. Diebler, *Ber. Bunsenges. Phys. Chem.*, **76**, 1035 (1972).

(7) Y. Sasaki and A. G. Sykes, *J. Chem. Soc., Chem. Commun.*, 767 (1973).

(8) J. D. Edwards, S. W. Foong, and A. G. Sykes, *J. Chem. Soc., Dalton Trans.*, 829 (1973).

(9) S. W. Foong and A. G. Sykes, *J. Chem. Soc., Dalton Trans.*, 504 (1973).

(10) K. L. Scott and A. G. Sykes, *J. Chem. Soc., Dalton Trans.*, 2364 (1972).

(11) S. W. Foong, R. D. Mast, M. B. Stevenson, and A. G. Sykes, *J. Chem. Soc. A*, 1266 (1971).

(12) M. B. Stevenson, A. G. Sykes, and R. S. Taylor, *J. Chem. Soc. A*, 3214 (1970).

(13) R. S. Taylor and A. G. Sykes, *J. Chem. Soc. A*, 1991 (1970).

(14) M. B. Stevenson, R. S. Taylor, and A. G. Sykes, *J. Chem. Soc. A*, 1059 (1970).

(15) S. W. Foong and A. G. Sykes, *J. Chem. Soc., Dalton Trans.*, 1453 (1974).

(16) See for example M. R. Hyde and A. G. Sykes, *J. Chem. Soc., Dalton Trans.*, 1583 (1974).

(17) S. W. Foong, M. B. Stevenson, and A. G. Sykes, *J. Chem. Soc. A*, 1064 (1970), and unpublished data.

(18) J. H. Espenson, *Inorg. Chem.*, **8**, 1554 (1969).

(19) R. Fuoss, *J. Amer. Chem. Soc.*, **80**, 5059 (1958).

(20) See also M. R. Hyde and A. G. Sykes, *J. Chem. Soc., Chem. Commun.*, 1340 (1972).

$$k'' = \frac{k_{HX}K_{HX}K_X[H^+][X^{n-}](1 + k_{HX_2}K_{HX_2}[X^{n-}]/k_{HX})}{1 + K_X[X^{n-}]} \qquad (4)$$

tor are small (which seems likely since $K_{HX} << 1$). It has been possible to demonstrate the effectiveness of k_{HX_2} and a denominator term $1 + K_X[X^{n-}]$ for bridge cleavage of the complex $(NH_3)_5Co\text{-}OH\text{-}Co(NH_3)_5{}^{5+}$,[21] where in this particular case there is a significant contribution from a pathway independent of $[H^+]$ and $[X^{n-}]$ which has proved advantageous. If therefore, for $(NH_3)_4Co\text{-}\mu(NH_2,OH)\text{-}Co(NH_3)_4{}^{4+}$, $k_{HX_2}K_{HX_2}/k_{HX} \approx K_X$, then (4) reduces to (5), which is con-

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

sistent with (2). Thus ion-pair formation may well be effective, even though a less than first-order dependence on $[X^{n-}]$ is not observed.

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_{ClO_4} are ion-pair forma-

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

tion constants for X^- and 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 $[Co(NH_3)_5H_2O]^{3+}$ by Cl^- and $SO_4{}^{2-}$ 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 $[X^-] + [ClO_4^-]$ is always con-

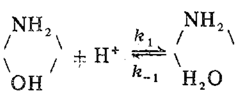
$$k = \frac{k'K_XK_{HX}}{1 + K_X([X^-] + [ClO_4^-])} \qquad (7)$$

stant at 2.0 M, this reduces to (8). The behavior observed is

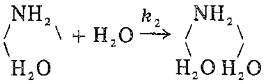
$$k = \frac{k'K_XK_{HX}}{1 + 2K_X} \qquad (8)$$

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.

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



(9)



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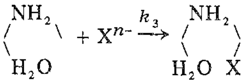

(11)

step. Assuming stationary-state kinetics for the five-coordinate intermediate k may be expressed as in (12). For our data to

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

be consistent with this $(k_{-1} + k_2[H_2O])$ must be $>> k_3[X^{n-}]$, and since we know that $k_3[X^{n-}] \geq k_2[H_2O]$, it follows that $k = k_3K_1$. This leads to a rather unsatisfactory conclusion that $k_{-1} >> k_2[H_2O]$ 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.

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.

(21) D. A. Buckingham, W. Marty, and A. M. Sargeson, *Inorg. Chem.*, 13, 2165 (1974); we are most grateful for correspondence from Dr. Sargeson.

(22) M. G. Burnett, *J. Chem. Soc. A*, 2480, 2486, 2490 (1970).

(23) R. K. Wharton and A. G. Sykes, *J. Chem. Soc., Dalton Trans.*, 439 (1973).

(24) J. D. Edwards, K. Wieghardt, and A. G. Sykes, to be submitted for publication in *J. Chem. Soc., Dalton Trans.*

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

AIC40276U

Sir:

In the course of our study[1-4] of cis and trans effects in the acid hydrolysis of complexes of the type *trans*-$[CoLACl]^{n+}$, where L = $(NH_3)_4$, $(en)_2$ (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^-, NO_2^-, NCS^-, CN^-, N_3^-, or 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.

(1) C. K. Poon, *Inorg. Chim. Acta, Rev.*, 4, 123 (1970).

(2) C. K. Poon, *Coord. Chem. Rev.*, 10, 1 (1973).

(3) C. K. Poon and H. W. Tong, *J. Chem. Soc., Dalton Trans.*, 1 (1974).

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

(5) L. P. Hammett, *Trans. Faraday Soc.*, 34, 156 (1938).

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