of dissolving gaseous Li^+ and F^-. Obviously the tightening effects of Li^+ on all F^- and of M^{4+} on the added one overcompensate the opposite effects and the same applies to Na^+F^-. However, for KF, RbF, NH_4F, and CsF, the cations of which exert a weaker polarizing field and have a larger polarizability than Li^+ and Na^+, the refractivity of A^+F^- in the complexes is larger than that of the gaseous ions.

On the whole, the absolute values of the above Δ for aqueous ions are only in the case of KF and NH_4 somewhat larger than Penneman's estimate of the standard deviations (average 0.11) given in his Table III. Hence, attempting to present his material from the simplified approximate point of view of additivity, Penneman was justified in choosing the refractivities of aqueous ions for comparison. Since F^- has the smallest polarizability among anions, the polarization effects in these complexes are relatively small. Nevertheless, they are clearly indicated by the signs of Δ derived from the comparison with gaseous ions. The irregular gradation of the absolute values of these Δ corresponds to their considerable standard deviations.

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RECEIVED MARCH 11, 1969

Formation Rates of Monosubstituted Chromium(III) Complexes in Aqueous Solution[1]

Sir:

The slow establishment of equilibrium in reaction I makes possible the evaluation of equilibrium and rate

$$Cr(H_2O)_6^{3+} + X^- = (H_2O)_5CrX^{2+} + H_2O \qquad (I)$$

parameters for the inner complexes $(H_2O)_5CrX^{2+}$. Following the approach of Seewald and Sutin[2] for iron(III) complexes, the formation rates[3] of the Cr(III) complexes will be considered in an attempt to establish some details of reaction mechanisms. A different but related approach to detailed mechanisms in these reactions has been taken by Swaddle and Guastalla,[4] who considered the correlation of aquation rates and stability quotients according to Langford's method.[5]

Complexes containing the strong-acid anions Cl^-, Br^-, I^-, ONO_2^-, SCN^-, and NCS^- form at rates given by the two-term rate expression

$$d[CrX^{2+}]/dt = [Cr^{3+}][X^-](a + (b/[H^+])) \qquad (1)$$

The two transition states are $[Cr(H_2O)_nX^{2+}]^{\ddagger}$ and $[Cr(H_2O)_n(OH)X^+]^{\ddagger}$. Assuming the latter corresponds to a prior acid dissociation of $Cr(H_2O)_6^{3+}$, followed by the reaction of Cr^{3+} and X^-, the second-order rate constant for the latter reaction can be computed using the known[6] acid dissociation quotient of $Cr(H_2O)_6^{3+}$, 1.3×10^{-4} *M*. The equilibrium and kinetic data refer to 25° and 1.00 *M* ionic strength; appropriate extrapolations were made in the cases where measurements were made under different conditions. The first part of Table I summarizes the values[7–19] of a and b/K_{Cr} for the six complexes considered.

The rates of formation of complexes containing anions of the weak acids HF and HN_3 are given by eq 2.

$$d[CrX^{2+}]/dt = [Cr^{3+}][HX](c + (d/[H^+])) \qquad (2)$$

The transition states so implicated are $[Cr(H_2O)_nHX^{3+}]^{\ddagger}$ and $[Cr(H_2O)_nX^{2+}]^{\ddagger}$. The first of these appears to be the substitution reaction of $Cr(H_2O)_6^{3+}$ and HX and can tentatively be ascribed to a mechanism similar to that for rate constant a. The second path is subject to two broad interpretations: reaction of $CrOH^{2+}$ and HX (similar to the reaction for b) or reaction of Cr^{3+} and X^- (similar to the reaction for a). In principle, both of the latter mechanisms operate to a finite extent, and the observed rate parameter d represents the sum of their contributions; kinetic studies will not differentiate the two pathways, however, since they correspond to transition states of the same composition. This constitutes a "proton ambiguity" in the mechanism.

In an attempt to advance some indirect arguments in favor of only one path making the dominant contribution to the observed rate term, it was first assumed the reaction of $CrOH^{2+}$ and HX was far more important than that of Cr^{3+} and X^- and then that the reverse approximation held. On such a basis, the second-order rate constants for each alternative can be computed, using known values of K_a for Cr^{3+},[6] HF,[20] and HN_3.[21] These rate constants are listed in the second part of Table I and are enclosed in parentheses to emphasize that both values do not apply simultaneously.

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(1) Work performed in the Ames Laboratory of the U.S. Atomic Energy Commission. Contribution No. 2453.

(2) D. Seewald and N. Sutin, *Inorg. Chem.*, **2**, 643 (1963).

(3) The formation (anation) rate constants for most complexes were computed from the aquation rates and the equilibrium quotient.

(4) T. W. Swaddle and G. Guastalla, *Inorg. Chem.*, **7**, 1915 (1968).

(5) C. H. Langford, *ibid.*, **4**, 265 (1965).

(6) C. Postmus and E. L. King, *J. Phys. Chem.*, **59**, 1208 (1955).

(7) (a) R. J. Baltisberger and E. L. King, *J. Am. Chem. Soc.*, **86**, 795 (1964); (b) C. F. Hale and E. L. King, *J. Phys. Chem.*, **71**, 1779 (1967).

(8) T. W. Swaddle and E. L. King, *Inorg. Chem.*, **4**, 532 (1965).

(9) J. H. Espenson and E. L. King, *J. Phys. Chem.*, **64**, 380 (1960).

(10) F. A. Guthrie and E. L. King, *Inorg. Chem.*, **3**, 916 (1964).

(11) M. Ardon and N. Sutin, *ibid.*, **6**, 2268 (1967); the value of k_{-1} cited therein is too small by a factor of 10. That error aside, the raw rate data in ref 11 and 12 are in good agreement.

(12) T. W. Swaddle, *J. Am. Chem. Soc.*, **89**, 4338 (1967).

(13) M. Orhanović and N. Sutin, *ibid.*, **90**, 4286 (1968).

(14) C. Postmus and E. L. King, *J. Phys. Chem.*, **59**, 1216 (1955). The anation rate of $CrNCS^{2+}$ also contains a minor term varying as $[H^+]^{-2}$, which would perhaps show up for other complexes as well were careful measurements at very low $[H^+]$ performed.

(15) The formation rate of $CrSCN^{2+}$ is based upon (1) its aquation rate,[13] (2) the equilibrium constant for the conversion of $CrSCN^{2+}$ to $CrNCS^{2+}$,[6,13] and (3) the rate constants for $CrNCS^{2+}$.[14]

(16) T. W. Swaddle and E. L. King, *Inorg. Chem.*, **3**, 234 (1964).

(17) J. H. Espenson and J. R. Pladziewicz, unpublished experiments.

(18) D. W. Carlyle and J. H. Espenson, *Inorg. Chem.*, **6**, 1370 (1967).

(19) The stability constant for CrN_3^{2+} was assumed to be equal to that of VN_3^{2+}; $Q = [VN_3^{2+}][H^+]/[V^{3+}][HN_3]$ which is *ca.* 0.04 at 25.0° and $\mu = 1.00$ *M*.[17] This is consistent with the observation that Cr(III) complexes are generally 10–30 times less stable than Fe(III) complexes, Q for FeN_3^{2+} being 0.51 under these conditions.[18]

(20) (a) R. P. Bell, K. N. Bascombe, and J. C. McCoubrey, *J. Chem. Soc.*, 1286 (1956); (b) L. G. Hepler, W. L. Jolly, and W. M. Latimer, *J. Am. Chem. Soc.*, **75**, 2809 (1953).

(21) E. A. Burns and F. D. Chang, *J. Phys. Chem.*, **63**, 1314 (1959).

TABLE I

SECOND-ORDER RATE CONSTANTS[a] FOR REACTIONS OF Cr^{3+} AND $CrOH^{2+}$ WITH VARIOUS ANIONIC AND NEUTRAL LIGANDS

	L	$Cr^{3+} + L$ 10^8k, M^{-1} sec^{-1}	$CrOH^{2+} + L$ 10^5k,[b] M^{-1} sec^{-1}	Ref
		Anions of Strong Acids		
$(H_2O)_5CrCl^{2+}$	Cl^-	3.0	2.3	*c, d*
$(H_2O)_5CrBr^{2+}$	Br^-	3.0	2.8	*e, f*
$(H_2O)_5CrI^{2+}$	I^-	0.08	0.26	*d, g*
$(H_2O)_5CrONO_2^{2+}$	NO_3^-	59	8.5	*h, i*
$(H_2O)_5CrSCN^{2+}$	SCN^-	0.41	0.49	*j, k–m*
$(H_2O)_5CrNCS^{2+}$	NCS^-	73	2.2	*j, l*
		Anions of Weak Acids		
$(H_2O)_5CrF^{2+}$	F^-	(1500)	...	*d*
	HF	22	(7.9)	
$(H_2O)_5CrN_3^{2+}$	N_3^-	(5900)	...	*n–q*
	HN_3	2.8	(1.9)	
		Special Cases		
$(H_2O)_5CrOSO_3^+$	SO_4^{2-}	(1600)	...	*r, s*
	HSO_4^-	2.6	(130)	
$(H_2O)_5CrOPH_2O^{2+}$	$H_2PO_2^-$	...	...	*t*
	H_3PO_2	2900	...	

[a] At 25.0°, $\mu = 1.00$ *M* with $HClO_4$ and $LiClO_4$ or $NaClO_4$. [b] Based on an acid dissociation constant of Cr^{3+} of 1.3×10^{-4} *M*.[6] [c] Reference 7. [d] Reference 8. [e] Reference 9. [f] Reference 10. [g] Reference 4. [h] Reference 11. [i] Reference 12. [j] Reference 6. [k] Reference 13. [l] Reference 14. [m] Reference 15. [n] Reference 16. [o] Reference 17. [p] Reference 18. [q] Reference 19. [r] N. Fogel, J. M. J. Tai, and J. Yarborough, *J. Am. Chem. Soc.*, **84,** 1145 (1962). [s] J. E. Finholt and J. N. Deming, *Inorg. Chem.*, **6,** 1533 (1967). [t] J. H. Espenson and D. E. Binau, *ibid.*, **5,** 1365 (1966); K. A. Schroeder and J. H. Espenson, *J. Am. Chem. Soc.*, **89,** 2548 (1967).

Excluding the parenthetic values, the six rate constants for $CrOH^{2+} + L$ lie in the range (0.26–8.5) $\times 10^{-5}$ M^{-1} sec^{-1}, or an even smaller range if NO_3^- is excluded (see below). The narrow spread of anation rates, considering a range of 10^{10} in stability, suggests that the rate of entry of various ligands to the primary coordination sphere may be controlled in each complex by largely the same factor.[2,18,22] The rate constants of the nine $Cr^{3+} + L$ reactions cover a range (0.08–73) $\times 10^{-8}$ M^{-1} sec^{-1}, a somewhat larger spread than noted for corresponding anations of Fe^{3+} [2,18,22,23] and $Co(NH_3)_5{}^{3+}$.[24] The larger spread of Cr^{3+} anation rates is to be expected, since for Cr^{3+} the slope of the log (k_{aq}) *vs.* log *Q* plot[4] (0.56) is considerably smaller than that of the similar plot[5] for $Co(NH_3)_5{}^{3+}$ (0.9).

The complexation reactions of chromium(III) appear to have a common rate-determining feature, ligand-assisted water loss (dissociative interchange[25]). The small ligand dependence of formation rates suggests that bond making does play a role in the mechanism and that the mechanism is not purely dissociative in character.

Arguments based on these observations may allow the "proton ambiguity" to be resolved in support of the proposals of Swaddle and King,[8,16] whose arguments were based on values of $\Delta S^{\ddagger}$. For both CrF^{2+} and CrN_3^{2+} there is a formation rate term $c[Cr^{3+}][HX]$, with rate constants whose values fall within the range cited for Cr^{3+} substitution. The rate coefficients for the second rate term, $d[Cr^{3+}][HX]/[H^+]$, when interpreted as being the reaction of $Cr(H_2O)_6{}^{3+}$ and X^-, are well outside the range ascribed to Cr^{3+} substitutions and, in fact, exceed the rate of Cr(III)–H_2O exchange.[26] To account for the values in such terms it would be necessary to invoke for these two anions special mechanisms inoperative for other anations or for solvent exchange. On the other hand, if this rate term is ascribed to the reaction of $(H_2O)_5CrOH^{2+}$ and HX, the values are in accord with the range of values found for other $CrOH^{2+}$ substitutions, as shown by the tabulated rate constants. It appears these reactions do proceed as concluded by Swaddle and King.[8,16] These conclusions are similar to those reached[2,18,27] for iron(III) substitutions with similar anions: the reactions of $FeOH^{2+}$ and HX were generally more important than those of $Fe(H_2O)_6{}^{3+}$ and X^-.

The usual effect of coordinated OH^- is to promote dissociative mechanisms through its π-bonding ability.[28] In accord, the narrower spread of the formation rates for substitution on $CrOH^{2+}$ than on Cr^{3+} should be noted.

The complexes $CrOPH_2O^{2+}$ and $CrOSO_3^+$ (and perhaps $CrONO_2^{2+}$) constitute special cases. The high reaction rate of Cr^{3+} and H_3PO_2 (third part of Table I) supports the suggestion[29] that complex formation may be governed by the rate of conversion of $HOPH_2O$ to $(HO)_2PH$.[30] The rate[31,32] of reaction of Cr^{3+} with

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(22) N. Sutin, *Ann. Rev. Phys. Chem.*, **17,** 119 (1966), and references therein.

(23) F. P. Cavasino, *J. Phys. Chem.*, **72,** 1378 (1968).

(24) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," 2nd ed, John Wiley & Sons, Inc., New York, N. Y., 1968, p 203.

(25) C. H. Langford and H. B. Gray, "Ligand Substitution Processes," W. A. Benjamin, Inc., New York, N. Y., 1965.

(26) R. A. Plane and J. P. Hunt, *J. Am. Chem. Soc.*, **76,** 5960 (1954); **79,** 3343 (1957).

(27) J. H. Espenson and S. R. Helzer, *Inorg. Chem.*, **8,** 1051 (1969).

(28) Reference 24, Chapter 3.

(29) (a) J. H. Espenson and D. E. Binau, *Inorg. Chem.*, **5,** 1365 (1966); (b) K. A. Schroeder and J. H. Espenson, *J. Am. Chem. Soc.*, **89,** 2548 (1967).

(30) The rate found[29a] for $Cr^{3+} + H_3PO_2$ appears consistent[29b] with the known general-acid catalysis of the tautomerism reaction, considering the acid strength of Cr^{3+}: W. A. Jenkins and D. M. Yost, *J. Inorg. Nucl. Chem.*, **11,** 297 (1959).

(31) N. Fogel, J. M. J. Tai, and J. Yarborough, *J. Am. Chem. Soc.*, **84,** 1145 (1962).

(32) J. E. Finholt and J. N. Deming, *Inorg. Chem.*, **6,** 1533 (1967).

HSO_4^- appears consistent with a simple anation reaction of Cr^{3+}, whereas the rate of $Cr^{3+} + SO_4^{2-}$ or $CrOH^{2+} + HSO_4^-$ may be set at sulfur, for the rate on either basis seems abnormally high. The charge type is different for this reaction, however, and it is not possible to claim that the sulfate reaction is really anomalous. Precedent for the suggestion of bond breaking at the nonmetal is found in the labile Cr(III) complexes formed by some oxy anions, notably $HCrO_4^-$ [33] and IO_3^-.[34]

The rate constant[12,13] for the reaction of Cr^{3+} and NO_3^- lies in the range of values for Cr^{3+} substitution, but considering its very feeble stability the rate is surprisingly high. This has been ascribed[35] to a possible nitrate–oxygen substitution, which appears to be a reasonable explanation.

Acknowledgment.—The author is indebted to Professors R. G. Pearson and T. W. Swaddle for helpful discussions and comments.

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[33] E. L. King and J. A. Neptune, *J. Am. Chem. Soc.*, **77**, 3186 (1955).

[34] N. V. Duffy and J. E. Earley, *ibid.*, **89**, 272 (1967).

[35] E. L. King as cited in ref 4.

[36] Fellow of the Alfred P. Sloan Foundation, 1968–1970.

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RECEIVED NOVEMBER 13, 1968

The Structures of Polyanions

Sir:

Although the formation of polymerized isopolyanions and heteropolyanions in aqueous solutions of vanadium(V), niobium(V), tantalum(V), molybdenum(VI), and tungsten(VI) is well known, a number of important questions remain unanswered.[1] These include why species of the same molecular weight are obtained in each case rather than a complex mixture of polymers, why the extent of polymerization is different for different metals, and what the reasons are for the adoption of the particular structures. Answers to these questions based solely on the size and charge of the metal atoms are presented in this correspondence.

Isopolyanions.—All known isopolyanion structures are constructed at least partly from MO_6 octahedra sharing edges. This introduces unfavorable Coulombic repulsions between the metal atoms, which can be partly accommodated by allowing the metal atoms to move away from the centers of their octahedral cages of oxygen atoms, which will be aided if the metal atom is relatively small. As the size of the polymer increases, it will become increasingly difficult for the electrostatic repulsion to be overcome by such distortion, until eventually polymerization by edge sharing of octahedra will cease. This Coulombic barrier will be reached later for the smaller ions,[2] that is, in the order V^{5+} ($r = 0.59$ Å) < Mo^{6+} ($r = 0.62$ Å) < W^{6+} ($r = 0.68$ Å) < Nb^{5+} ($r = 0.70$ Å) < Ta^{5+} ($r = 0.73$ Å). (This order also parallels the degree of distortion in the oxides.) This order is in agreement with experiment where it is found that the ions formed by edge sharing of octahedra (in contrast to the larger corner-sharing paratungstate Z and metatungstate) are $V_{10}O_{28}^{6-}$, $Mo_8O_{26}^{4-}$ and $Mo_7O_{24}^{6-}$, $HW_6O_{21}^{5-}$ (assuming an edge-shared structure), $Nb_6O_{19}^{8-}$, and $Ta_6O_{19}^{8-}$.

The shapes of the polyanions can also be predicted. If a third octahedron is added to a pair of edge-shared octahedra, the M–M–M angle can be 60, 90, 120, or 180° depending upon the particular edges shared by the central octahedron. The last two cases will be less favorable as the central metal atom is subjected to opposing Coulombic forces, which cannot be readily relieved by distortion. The 60° interaction is clearly the most favorable, and this is the edge-shared structural unit found in metatungstate $H_2(W_3O_{10})_4^{6-}$ and in many heteropolymolybdates and heteropolytungstates.[3]

For four octahedra sharing edges the two most favorable structures are shown in Figure 1. The approximately tetrahedral structure of M_4O_{16} is the most favorable as it again involves only 60° M–M–M interactions, and this is the structure found in $Li_{14}(WO_4)_3(W_4O_{16}) \cdot 4H_2O$.[4] All other structures (about 20) involve unfavorable 180 or 120° interactions or more of the moderately unfavorable 90° interactions than occur in M_4O_{18}.

For six octahedra sharing edges, there are only two structures which avoid the unfavorable 180 or 120° interactions (Figure 2). The first is M_6O_{19} which has the six metal atoms in an octahedral arrangement and is the structure observed for $Nb_6O_{19}^{8-}$ and $Ta_6O_{19}^{8-}$.[5] The second is M_6O_{26} which is a continuation of the M_4O_{18} structure. This zigzag polymerization can continue indefinitely without encountering any Coulombic barrier and would result in a complex distribution of high molecular weight polymers. The reason these structures are not observed must be the very favorable entropy change accompanying elimination of water molecules with the formation of more compact structures, for example, M_6O_{19} from M_6O_{26}.

For more than six octahedra sharing edges, some of the unfavorable 120 or 180° M–M–M interactions become inevitable. The largest of the isopolyanions, $V_{10}O_{28}^{6-}$ (Figure 3), has two such 180° interactions, but the structure is considerably distorted due to mutual repulsion of the vanadium atoms so that the vanadium–oxygen bonds range from 1.59 to 2.22 Å, and the central V–V–V angles are reduced from 180 to 175°.[6] The

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[1] For example, see C. S. G. Phillips and R. J. P. Williams, "Inorganic Chemistry," Vol. 1, Oxford University Press, London, 1965.

[2] "Table of Periodic Properties of the Elements," E. H. Sargent and Co., Chicago, Ill., 1965.

[3] D. L. Kepert, *Progr. Inorg. Chem.*, **4**, 199 (1962).

[4] A. Hullen, *Naturwissenschaften*, **51**, 508 (1964); K. F. Jahr and J. Fuchs, *Angew. Chem. Intern. Ed. Engl.*, **5**, 689 (1966).

[5] I. Lindqvist, *Arkiv Kemi*, **5**, 247 (1953); I. Lindqvist and B. Aronsson, *ibid.*, **7**, 49 (1955).

[6] H. T. Evans, A. G. Swallow, and W. H. Barnes, *J. Am. Chem. Soc.*, **86**, 4209 (1964); A. G. Swallow, F. R. Ahmed, and W. H. Barnes, *Acta Cryst.*, **21**, 397 (1966); H. T. Evans, *Inorg. Chem.*, **5**, 967 (1966).