formation of $(C_6H_5)_2PNHNH_3Cl$. This could then be followed by an Arbuzov-type rearrangement, similar to that suggested by Winyall and Sisler[5] in the polymerization of 2,2-dimethylhydrazinodiphenylphosphine, to give $[(C_6H_5)_2P(NH_2)_2]Cl$. Intermolecular condensation of this intermediate with the elimination of NH_4Cl would be expected to yield $[NH_2(P(C_6H_5)_2{=}N)_nH_2]Cl$ and cyclic products $[(C_6H_5)_2P{=}N]_n$ as indicated by Sisler, *et al.*,[1] in the reaction of diphenylchlorophosphine with ammonia–chloramine mixtures. However, his mechanism is not entirely satisfactory since it does not explain why the reaction proceeds to a longer chain length moiety rather than stopping at the stable $[NH_2(P(C_6H_5)_2{=}N)_2H_2]Cl$.

The optimum conditions for the formation of $[NH_2(P(C_6H_5)_2{=}N)_3H_2]Cl$ appear to be long reaction times at moderate temperatures. In all experiments incomplete reaction was observed as evidenced by isolation of unreacted hydrazine hydrochloride and/or isolation of the oxidative hydrolysis product of diphenylchlorophosphine, namely, $(C_6H_5)_2POOH$. At temperatures below 145° no evidence of reaction was obtained, whereas at high temperature only cyclic polymers were isolated.

The linear compound $ClP(C_6H_5)_2{=}NP(C_6H_5)_2NH$ reported by Sisler, *et al.*,[1] was not detected in this work nor has a satisfactory mechanism for its formation been proposed. Furthermore, it would be expected that such a compound would hydrolyze readily owing to the presence of a labile chlorine atom. This compound would be analogous to $ClP(C_6H_5)_2{=}NP(C_6H_5)_2{=}O$ postulated as a product of the reaction between diphenylchlorophosphine and diphenylphosphenyl azide by Paciorek[6] which was isolated only as the hydrolysis product, $(C_6H_5)_2P(O)NHP(O)(C_6H_5)_2$. However, other evidence for this type of compound does exist. Bunting and Schmulbach[7] have reported the preparation of the next lower homolog, chlorodiphenylphosphinimine, $ClP(C_6H_5)_2NH$, which they found polymerizes to diphenylphosphonitrile tetramer on pyrolysis and hydrolyzes to diphenylphosphinic acid.

Pyrolysis of $[NH_2(P(C_6H_5)_2{=}N)_3H_2]Cl$ was found to yield diphenylphosphonitrile trimer. This is probably due to intramolecular condensation with the elimination of NH_4Cl, whereas in the case of the next lower homolog intermolecular condensation probably takes place yielding mainly the tetramer.[1] Likewise pyrolysis of $ClP(C_6H_5)_2{=}NP(C_6H_5)_2NH$ would be expected to yield the tetramer by intermolecular elimination of HCl rather than the trimer as reported for the compound tentatively assigned this structure.

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[5] M. Winyall and H. H. Sisler, *Inorg. Chem.*, **4**, 655 (1965).

[6] K. L. Paciorek, *ibid.*, **3**, 96 (1964).

[7] R. K. Bunting and C. D. Schmulbach, *ibid.*, **5**, 533 (1966).

Correspondence

Comments on the Article by R. A. Penneman

Sir:

Dr. Robert A. Penneman asked me to comment on his article "Molar Refractivity as a Diagnostic Tool for Determining Composition of Transition Element Fluoride Complexes," which is published on page 1379 of the present issue. An interesting correspondence developed which led to a mutual understanding of our somewhat different approaches to this kind of problem. The following remarks explain the situation.

The molar refractivity of the complexes is considered by Penneman to be additive according to the equation

$$R_{nAF\cdot MF_4} = nR_{(A^+ + F^-)} + R_{MF_4}$$

Since the complexes as well as the MF_4 compounds are crystalline, additivity would imply that the values valid for gaseous ions are employed for R_{A^+} and R_{F^-}. However, the absolute values (in cm³) of the following differences Δ between, on the one hand, the average refractivities R_{cc} which the six fluorides have in the complexes according to Penneman's Table III and the values which their ions have (see footnote *a* to Penneman's Table III) in the aqueous or gaseous state are smaller (with the exception of NH_4F) for the aqueous ions.

TABLE I

DIFFERENCES BETWEEN THE REFRACTIVITIES (IN CM³) OF FLUORIDES IN THE COMPLEXES AND OF THEIR AQUEOUS OR GASEOUS IONS

Δ	LiF	NaF	KF	RbF	NH_4F	CsF
$R_{co} - R_{aq}$	+0.06	−0.10	+0.12	−0.03	−0.13	+0.03
$R_{co} - R_g$	−0.18	−0.22	+0.28	+0.13	+0.03	+0.19

The reason for distinguishing the values R_g and R_{aq} for Li^+, Na^+, and F^-, which have the largest energies of hydration, is as follows. According to a general principle,[1] cations (anions) tighten (loosen) the electronic system of neighboring anions (cations) and neutral molecules, *i.e.*, diminish (increase) their refractivity. For instance, the small Li^+ in aqueous solution decreases the refraction of the surrounding water by 0.40, while F^- increases it by 0.16. When 1 mol of gaseous Li^+ and F^- combines with $M^{4+}F^-{}_4$, a number of positive and negative effects occur and it is more or less accidental that the total effect (−0.18) comes close to that (−0.24)

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[1] K. Fajans and G. Joos, *Z. Phys.*, **23**, 1 (1924).

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).