

isotope effect in the autoprotolysis constant of water ( $K_{\text{H}_2\text{O}}/K_{\text{D}_2\text{O}} = 6.5^{19}$ ).

### Conclusions

The similarity of Pd(II) to Pt(II) which is seen in the discussion above implies that the mechanism of Pd(II) substitution reactions is the same as for Pt(II), at least in the gross features. Edwards and Pearson<sup>20</sup> have discussed a model for nucleophilic reactivities in terms of the basicity and polarizability of the entering nucleophile. Analysis of the data for Pt(II) has led to the observation that the dominant feature is polarizability. For Pd(II) the increasing rates of substitution  $\text{H}_2\text{O} < \text{Cl}^- < \text{Br}^- < \text{I}^- < \text{SCN}^-$  suggest that polarizability is also the important factor in determining nucleophilic reactivity. For Pt(dien)Br<sup>+</sup> the relative reactivities are given as  $1:2 \times 10^3:1 \times 10^4$  for  $\text{H}_2\text{O}$ ,  $\text{Cl}^-$ , and  $\text{Br}^-$ . For Pd(acac)<sub>2</sub>, the relative reactivities are  $1:1.5 \times 10^2:4 \times 10^2$ . For both Pt(II) and Pd(II), hydroxide ion is a poor nucleophile.

It is interesting to compare the data for the relative *trans* effect of  $\text{Cl}^-$  and  $\text{Br}^-$  in Pt(II) to that estimated for Pd(II) in this work. For Pt(II), the relative *trans* effect of  $\text{Br}^-$  vs.  $\text{Cl}^-$  shows a threefold increase in the rate of *trans* substitution.<sup>21</sup> For Pd(acac)X<sub>2</sub> the relative *trans* effect of  $\text{Br}^-$  vs.  $\text{Cl}^-$  is estimated to be 10:1.

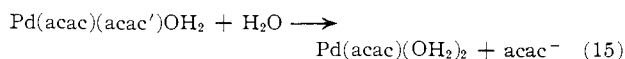
(19) R. W. Kingerley and V. K. La Mer, *J. Am. Chem. Soc.*, **63**, 3256 (1941).

(20) J. O. Edwards and R. G. Pearson, *ibid.*, **84**, 16 (1962).

(21) O. E. Zvyagintsev and E. F. Karandasheva, *Dokl. Akad. Nauk SSSR*, **101**, 93 (1955).

This larger ratio is somewhat surprising. Earlier, very fragmentary evidence<sup>4</sup> suggested that while a *trans* effect existed for palladium(II), it was of less importance than in the case of platinum(II).

The data of Table I and particularly Table II, where lower concentrations of hydrogen ion could be used, show that the rate of dissociation of Pd(acac)<sub>2</sub> goes to zero as  $[\text{H}^+]$  goes to zero. Table IV shows also that the rate goes to zero as  $[\text{OH}^-]$  goes to zero. Thus the dissociation of the intermediate I'



has a negligible rate compared to the reclosing of the chelate ring governed by  $k_{-1}$ . It is precisely this ratio of the rate of closing of the ring compared to dissociation which creates the extra stability of a chelate ligand compared to a unidentate ligand.<sup>22</sup> For other bidentate chelates such as ethylenediamine and glycine, this ratio is about 20–30.<sup>23</sup> The corresponding ratio for the anion of acetylacetonate must be greater than 100. Consequently, a very large chelate effect exists.

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(22) See ref. 2a, p. 18, for a discussion of the chelate effect.

(23) A. K. S. Ahmed and R. G. Wilkins, *J. Chem. Soc.*, 2901 (1960); G. G. Hammes and J. I. Steinfeld, *J. Am. Chem. Soc.*, **84**, 4639 (1962).

[CONTRIBUTION FROM THE DEPARTMENTS OF CHEMISTRY OF THE UNIVERSITY OF WISCONSIN, MADISON, WISCONSIN, AND THE UNIVERSITY OF COLORADO, BOULDER, COLORADO]

## The Solvation of Chromium(III) Ion in Acidic Water–Methanol Mixed Solvents<sup>1,2</sup>

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The low rate of exchange of solvent molecules between the first coordination shell of solvated chromium(III) ion and the solvent allows evaluation of  $\bar{n}$ , the average number of methanol molecules bound per chromium(III) ion, as a function of solvent composition in acidic water–methanol solutions. The data indicate that with respect to first shell coordination chromium(III) ion discriminates in favor of water over methanol. At 60°,  $\bar{n}$  ranges from 0.17 at  $Z_{\text{MeOH}} = 0.155$  to 3.60 at  $Z_{\text{MeOH}} = 0.98$ . (The mole fraction of methanol calculated without account being taken of solute species is  $Z_{\text{MeOH}}$ .) Values of  $\bar{n}$  at 30° are only very slightly lower. An independent type of experiment allowed evaluation of the fraction of chromium(III) present as hexaquo-chromium(III) ion. This quantity evaluated in solvents as rich in methanol as  $Z_{\text{MeOH}} = 0.85$  is consistent with the  $\bar{n}$  data. Equilibrium constants for the stepwise replacement of water by methanol in  $\text{Cr}(\text{OH}_2)_{6-j}(\text{OHMe})_j^{3+}$  have been calculated from the  $\bar{n}$  data.

This paper describes experiments on the inner-sphere solvation of chromium(III) ion in the mixed solvent, water–methanol. The success of these experiments depends upon the low rate of exchange of solvent molecules between the first coordination shell of solvated chromium(III) ion and the solvent, analogous to the low rate of exchange of water molecules between the first coordination shell of hydrated chromium(III) ion and solvent water in aqueous solution.<sup>4</sup> Two types of

experiments were performed. The average number of methanol molecules bound per chromium(III) ion,  $\bar{n}$ , was evaluated after using an ion-exchange procedure to separate chromium(III) ion with its methanol-containing coordination shell from the parent solvent. An ion-exchange procedure was used also in the second type of experiment to separate hexaquo-chromium(III) ion from the mixture of aquomethanol–chromium(III) species present at equilibrium in solutions in the mixed solvents. With an isotopic dilution procedure establishing the extent of recovery of hexaquo-chromium(III) ion, the fraction of chromium(III) present as hexaquo-chromium(III) ion,  $\alpha_0$ , was accessible.

The relationships of these two functions  $\bar{n}$  and  $\alpha_0$  to the concentrations of species  $\text{Cr}(\text{OH}_2)_{6-j}(\text{OHMe})_j^{3+}$

(1) Taken from the Ph.D. thesis of Jerrold C. Jayne, University of Wisconsin, 1963. Presented at the Solvation Symposium sponsored by the Chemical Institute of Canada at Calgary, Alberta, August 29, 1963.

(2) This work was supported in part by the Research Committee of the Graduate School, University of Wisconsin, the United States Atomic Energy Commission (Contract AT-(11-1)-1168 (U. of Wisconsin)), and the National Science Foundation (Grant GP-680 (U. of Colorado)).

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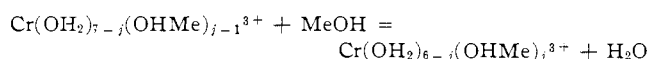
(4) J. P. Hunt and H. Taube, *J. Chem. Phys.*, **19**, 602 (1951).

are

$$\bar{n} = \frac{\sum j [\text{Cr}(\text{OH}_2)_{6-j}(\text{OHMe})_j^{3+}]}{\sum [\text{Cr}(\text{OH}_2)_{6-j}(\text{OHMe})_j^{3+}]} \quad (1)$$

$$\alpha_0 = \frac{[\text{Cr}(\text{OH}_2)_6^{3+}]}{\sum [\text{Cr}(\text{OH}_2)_{6-j}(\text{OHMe})_j^{3+}]} \quad (2)$$

Values of  $\bar{n}$  were obtained at 60° for solutions to 98.2 mole % methanol and at 30° for solutions to 96.3 mole % methanol. Values of  $\alpha_0$  were obtained at 60° to 85.3 mole % methanol. (Throughout this paper, the presence of solutes will not be taken into account in calculating the solvent composition.) The quantities  $\bar{n}$  and  $\alpha_0$  are of interest in themselves, but their interest is enhanced since, within the framework of simplifying assumptions, their dependence upon solvent composition allows calculation of the equilibrium quotients for the reactions



with  $j = 1, 2, \dots$

### Experimental

**Reagents.**—All solutions were prepared using reagent grade methanol and doubly-distilled water, the second distillation being from alkaline permanganate solution using a Barnstead still. The water content of reagent grade methanol was determined from measurement of its density. Chromium(III) perchlorate was prepared from reagent grade potassium dichromate by the reaction of hydrogen peroxide and chromium(VI) in perchloric acid solution. Chromium(III) perchlorate ( $\text{Cr}(\text{ClO}_4)_3 \cdot 9\text{H}_2\text{O}$ ) was crystallized from the reaction solution and then recrystallized three times from 1 *M* perchloric acid solution. In this procedure, potassium perchlorate was removed almost completely. From the light absorption in the region of 230  $m\mu$ , the stock solutions of chromium(III) perchlorate were judged to be essentially free of dimeric species.<sup>5</sup> Chromium-51 was obtained in the form of chromium(III) chloride in hydrochloric acid from the Oak Ridge National Laboratory.

Ion-exchange procedures involved use of Dowex-50W-X-12 200–400 mesh cation-exchange resin (J. T. Baker): which was treated before use by a sequence of reagents, hydrochloric acid, sodium citrate, hydrochloric acid, sodium hydroxide, hydrochloric acid, and perchloric acid.<sup>6</sup>

**Analytical Procedures.**—Analytical procedures involved use of primary standard potassium dichromate, reagent grade sodium hydroxide, cerium(IV) solutions in sulfuric acid prepared from ammonium hexanitratocerate (G. F. Smith), and iron(II) sulfate solutions prepared from either reagent grade iron(II) sulfate or iron(II) ammonium sulfate.

Analyses for chromium, in both stock solutions and equilibrated solutions, were performed by treatment with hydrogen peroxide and excess base followed by measurement of light absorption at 372  $m\mu$ , where chromate ion has an absorbancy index of  $4.85 \times 10^3$  l. mole<sup>-1</sup> cm.<sup>-1</sup>. The concentration of hydrogen ion in chromium(III) perchlorate-perchloric acid stock solutions was determined by titration with standard base after first complexing chromium(III) with excess oxalate ion.<sup>7</sup> The total normality of the stock solutions was determined by titration of the acid in the combined effluent solution and rinses after an aliquot of solution had passed through a column of cation-exchange resin in the hydrogen ion form.

The methanol content of aqueous solutions of aquomethanol-chromium(III) species was determined by oxidizing methanol to carbon dioxide with cerium(IV), using chromium(VI) as a catalyst. The procedure, suggested by an analytical method for formic acid,<sup>8</sup> required a fourfold excess of oxidant and ~11 *M* sulfuric acid. The heat of mixing which developed with addition

of concentrated sulfuric acid to give this acidity raised the temperature to ~110°, and this was sufficient to cause reaction to go to completion during the time required for the solution to cool before titration.

The radioactivity of eluent portions was determined with a scintillation counter coupled with a  $\gamma$ -ray spectrometer.

### Results

**$\bar{n}$  Experiments.**—Solutions containing water, methanol, chromium(III) perchlorate, and perchloric acid were prepared by combined use of volumetric ware and gravimetric measurements to give solute molarities and mole fraction composition of the solvent. These solutions were equilibrated in closed Pyrex vessels at 60° for 7 hr. or more (in many cases for much longer periods of time) and at 30° for 130 days. These equilibration times were proved to be more than adequate by measurements of  $\bar{n}$  as a function of time, by studies in which the equilibrium value of  $\bar{n}$  was approached from too high a value, and by independently obtained kinetic data.<sup>9</sup>

Following equilibration, 10 to 50 ml. of solution was chilled and poured through a jacketed column of cation-exchange resin maintained close to 0° (in a few experiments, the temperature was as high as 8°). Chromium(III) ion went into the resin phase under these conditions, and the column was rinsed with chilled aqueous 0.03 *M* sulfuric or perchloric acid. This rinsing, requiring 3–6 hr., removes solvent methanol but does not elute chromium(III) species. The duration of rinsing was selected to minimize errors due both to incomplete removal of solvent methanol from the column and to a quation of aquomethanol-chromium(III) species during rinsing.<sup>10</sup> Following the rinsing, 96–100% of the chromium(III) ion with its first coordination shell intact was eluted from the column with 2–3 *M* sulfuric acid. This eluent was analyzed for chromium and methanol by the methods already described. These data allow calculation of  $\bar{n}$  values which are given as a function of solvent composition in Tables I and II. The solvent composition is expressed in two ways, as  $Z_{\text{MeOH}}$ , the mole fraction of methanol, in the calculation of which the presence of solutes is not taken into account, and also as  $r$ , the ratio of moles of free methanol to moles of free water in the solvent, in the calculation of which correction was made for the amount of water tied up by chromium(III) ion ( $(6 - \bar{n})$  moles per mole of chromium(III) ion) and hydrogen ion (1 mole per mole of hydrogen ion). In making this correction for binding of one water molecule per hydrogen ion, it is assumed first that water is more basic than methanol and second that hydronium ion does not discriminate between water and methanol in its next shell. The uncertainty in the value of  $r$  arises largely from uncertainty in the water content of the methanol used in preparing the solutions. The values of  $\bar{n}$  are uncertain by 0.5–2.0%.

At the highest methanol concentration, complications appeared in experiments of long duration at 60°. In such experiments, the value of  $\bar{n}$  decreased at long times, and part of the chromium(III) ion was eluted from the ion-exchange resin with greater difficulty. The value of  $\bar{n}$  reported for such an experiment is the maximum value. It seems reasonable to interpret this

(9) R. J. Baltisberger and E. L. King, *J. Am. Chem. Soc.*, **86**, 795 (1964).

(10) An uncertain extrapolation of the rate constants reported in ref. 9 indicates the half-time for a quation of methanolpentaquochromium(III) ion at 4° to be 10<sup>4</sup> hr.

(5) J. A. Laswick and R. A. Plane, *J. Am. Chem. Soc.*, **81**, 3564 (1959).

(6) W. Rieman, III, and A. E. Breyer, "Chromatography: Columnar Liquid-Solid Ion Exchange Processes," in "Treatise on Analytical Chemistry," Part I, Vol. III, I. M. Kolthoff, et al., Ed., Interscience Publishers, New York, N. Y., 1961, p. 1556.

(7) W. J. Blaedel and J. J. Panos, *Anal. Chem.*, **22**, 910 (1950).

(8) N. N. Sharma and R. C. Mehrotra, *Anal. Chim. Acta*, **13**, 420 (1955).

TABLE I  
EQUILIBRIUM VALUES OF  $\bar{n}$  AT 60°  
0.010 *M* Cr(ClO<sub>4</sub>)<sub>3</sub>, 0.10 *M* HClO<sub>4</sub><sup>a</sup>

Z <sub>MeOH</sub>	<i>r</i>	$\bar{n}$	Z <sub>MeOH</sub>	<i>r</i>	$\bar{n}$	Z <sub>MeOH</sub>	<i>r</i>	$\bar{n}$
0.154	0.182 <sup>d</sup>	0.169	0.722	2.64 <sup>d</sup>	1.01	0.954 <sup>e</sup>	23 <sup>j</sup>	2.72
0.155	0.185 <sup>d</sup>	0.174	0.818	4.62 <sup>h</sup>	1.31	0.959 <sup>b</sup>	25 <sup>j</sup>	2.68
0.302	0.435 <sup>f</sup>	0.334	0.854	6.06 <sup>h</sup>	1.52	0.964	31 <sup>i</sup>	2.78
0.355	0.552 <sup>j</sup>	0.393	0.855 <sup>c</sup>	6.10 <sup>f</sup>	1.56	0.965 <sup>c</sup>	36 <sup>j</sup>	2.89
0.412 <sup>b</sup>	0.705 <sup>f</sup>	0.462	0.882 <sup>c</sup>	8.06 <sup>h</sup>	1.74	0.966 <sup>c</sup>	38 <sup>j</sup>	2.96
0.453	0.836 <sup>f</sup>	0.529	0.892	8.6 <sup>i</sup>	1.82	0.974 <sup>e</sup>	45 <sup>j</sup>	3.14
0.499	1.006 <sup>d</sup>	0.58	0.897 <sup>b</sup>	9.0 <sup>h</sup>	1.82	0.975	48 <sup>j</sup>	3.31
0.498 <sup>c</sup>	1.008 <sup>d</sup>	0.584	0.924 <sup>e</sup>	12.7 <sup>i</sup>	2.10	0.980 <sup>d</sup>	55 <sup>j</sup>	3.53
0.566	1.314 <sup>d</sup>	0.70	0.931	14.5 <sup>i</sup>	2.18	0.981 <sup>b</sup>	64 <sup>j</sup>	3.6
0.627	1.70 <sup>d</sup>	0.77	0.943 <sup>c</sup>	19.5 <sup>i</sup>	2.38	0.982 <sup>b</sup>	65 <sup>j</sup>	3.60
0.685 <sup>b</sup>	2.19 <sup>f</sup>	0.91	0.953	22 <sup>j</sup>	2.60			

<sup>a</sup> Unless otherwise noted. <sup>b</sup> 0.05 *M* HClO<sub>4</sub>. <sup>c</sup> 0.20 *M* HClO<sub>4</sub>. <sup>d</sup> 0.0025 *M* Cr(ClO<sub>4</sub>)<sub>3</sub>, 0.05 *M* HClO<sub>4</sub>. <sup>e</sup> 0.003 *M* Cr(ClO<sub>4</sub>)<sub>3</sub>, 0.116 *M* HClO<sub>4</sub>. <sup>f</sup> Uncertainty in value of *r* is <0.5%. <sup>g</sup> Uncertainty in value of *r* is 0.5–1.0%. <sup>h</sup> Uncertainty in value of *r* is 1.0–2.0%. <sup>i</sup> Uncertainty in value of *r* is 2.0–4.0%. <sup>j</sup> Uncertainty in value of *r* is 4.0–8.0%.

behavior to mean that polynuclear species involving Cr–O–Cr bonding form very slowly under these conditions. Such species, analogous to those in aqueous

TABLE II  
EQUILIBRIUM VALUES OF  $\bar{n}$  AT 30°  
0.010 *M* Cr(ClO<sub>4</sub>)<sub>3</sub>, 0.10 *M* HClO<sub>4</sub>

Z <sub>MeOH</sub>	<i>r</i>	$\bar{n}$
0.146	0.172 <sup>a</sup>	0.147
0.296	0.422 <sup>a</sup>	0.291
0.392	0.649 <sup>a</sup>	0.414
0.615	1.62 <sup>a</sup>	0.712
0.625	1.69 <sup>a</sup>	0.771
0.718	2.58 <sup>b</sup>	0.95
0.738	2.87 <sup>b</sup>	1.01
0.779	3.59 <sup>b</sup>	1.15
0.840	5.4 <sup>b</sup>	1.32
0.922	12.5 <sup>c</sup>	1.92
0.938	16.4 <sup>c</sup>	2.12
0.954	24 <sup>c</sup>	2.33
0.963	30 <sup>c</sup>	2.46

<sup>a</sup> Uncertainty in value of *r* is <1%. <sup>b</sup> Uncertainty in value of *r* is 1–2%. <sup>c</sup> Uncertainty in value of *r* is 4–10%.

solution studied by Laswick and Plane,<sup>5</sup> probably would have a net charge greater than 3+ and would contain fewer methanol molecules per chromium(III) than are contained in mononuclear species. The best evidence that chromium(III) species in equilibrated solutions are predominantly monomeric is their elution behavior. Except in those experiments at the highest methanol concentration which were equilibrated for excessive periods of time, the elutability of chromium(III) and its almost quantitative recovery indicate dimeric species<sup>5</sup> are essentially absent. It cannot be asserted, of course, that dimers or higher polymers are not present to an appreciable extent under more favorable concentration conditions or in solutions heated for very much longer periods of time.

The values of  $\bar{n}$  obtained in this study agree very well with those from a more limited study at ionic strength 0.418 *M*.<sup>9</sup> Only at the highest methanol concentrations common to the two studies (*Z*<sub>MeOH</sub> = 0.7) is there an appreciable difference; the slight increase in  $\bar{n}$  with increase in ionic strength at a particular *Z*<sub>MeOH</sub> is consistent with preferential solvation of sodium ion and/or perchlorate ion by water. The resultant salting out of methanol by sodium perchlorate would raise the value of  $\bar{n}$ . That neither perchlorate ion nor hydroxide ion discriminates strongly between water and

methanol is indicated by the general consistency of data taken in the present study at 0.050, 0.10, and 0.20 *M* perchloric acid. In the calculation of *r*, preferential solvation of the proton by one water molecule is taken into account; the strong interaction of hydronium ion with three additional solvent molecules<sup>11</sup> is assumed to involve inappreciable discrimination.

**α<sub>0</sub>-Experiments.**—Hexaaquochromium(III) ion is more easily eluted from cation-exchange resin than chromium(III) species containing one or more coordinated methanol molecules. This provides the basis for evaluation of the relative concentration of hexaaquochromium(III) ion in equilibrated water-methanol solutions of chromium(III) perchlorate and perchloric acid. After equilibration, solutions of chromium(III) perchlorate in acidified mixed solvent were diluted with a chilled aqueous acidic solution of hexaaquochromium(III) ion. Either the equilibrated solution in the mixed solvent or the diluting aqueous solution contained chromium-51 of known specific activity. The combined solution was poured through a jacketed column of cation-exchange resin where all chromium(III) species were taken into the resin phase. Slow elution with chilled 2 *M* perchloric acid followed. Successive fractions were collected for both chromium analysis and determination of radioactivity. That hexaaquochromium(III) ion is more easily eluted than other solvated chromium(III) species was demonstrated by the constant specific activity of early eluent portions in experiments in which the diluting solution was tagged, this constant specific activity being lower than that of hexaaquochromium(III) ion in the diluting solution. In an experiment with *Z*<sub>MeOH</sub> = 0.444 the specific activity of five successive early eluent portions was (in arbitrary units) 84.2, 81.5, 82.2, 81.6, and 82.4. The specific activity of the next five portions was 79.6, 80.5, 79.2, 75.9, and 73.4, and the specific activity of the diluting solution was ~1.0 × 10<sup>6</sup>. Fourteen per cent of the hexaaquochromium(III) ion was present in the five early eluent portions of constant specific activity.<sup>12</sup>

(11) R. P. Bell, "The Proton in Chemistry," Cornell University Press, Ithaca, N. Y., 1959, Chapters 3 and 6.

(12) Since the tracer solution contained chloride ion, a small amount of chlorochromium(III) ion was present in the tagged solution. Those species with charge ≤2+ were eluted completely before species of charge 3+ (i.e., the species of interest, Cr(OH)<sub>2</sub>(s-j)(OHMe)<sub>j</sub><sup>3+</sup>). In all calculations, account was taken of the chromium and radioactivity tied up as chlorochromium(III) species.

In typical experiments of this type, 6–7 ml. of resin was used in a column of  $\sim 3$  cm. length. The time elapsed from the time of mixing the equilibrium and diluting solutions together to the time of elution of the fractions containing only hexaaquochromium(III) ion was 2.5–3.7 hr. At the temperatures employed in this procedure ( $\sim 4^\circ$ ), inappreciable aquation of methanol-pentaquochromium(III) ion occurred during this time interval.<sup>9,13</sup> If species containing more than one methanol aquate at a higher rate, the last aquation step  $\text{Cr}(\text{OH}_2)_5\text{OHMe}^{3+} + \text{H}_2\text{O} = \text{Cr}(\text{OH}_2)_6^{3+} + \text{MeOH}$  would be a barrier to formation of hexaaquochromium(III) ion, and the value of  $\alpha_0$  would be correct despite occurrence of all stages of aquation except the last.

From the known amounts of chromium present in both equilibrium and diluting solutions and the specific activity of chromium in both the eluted hexaaquochromium(III) ion and the solution originally tagged, the value of  $\alpha_0$  can be calculated. The equations, derivable in a direct manner, are

$$\alpha_0 = \left( \frac{S_h}{S_{\text{eq}} - S_h} \right) \frac{n_d}{n_{\text{eq}}} \quad (3)$$

if the equilibrium solution is tagged, and

$$\alpha_0 = \frac{S_d}{S_h} \left( \frac{n_d}{n_d + n_{\text{eq}}} \right) \quad (4)$$

if the diluting solution is tagged, where  $S_h$ ,  $S_{\text{eq}}$ , and  $S_d$  are specific activities of chromium in hexaaquochromium(III) ion, equilibrium solution, and diluting solution, respectively, and  $n_{\text{eq}}$  and  $n_d$  are the numbers of moles of chromium(III) in the equilibrium solution and the diluting solution, respectively. Values of  $\alpha_0$  calculated by use of these equations applied to data of seven experiments are presented in Table III.

TABLE III  
EQUILIBRIUM VALUES OF  $\alpha_0^a$

$Z_{\text{MeOH}}$	$r$	$\alpha_0$
0.171	0.207	0.83
0.444	0.805	0.63
0.542 <sup>b</sup>	1.192	0.54
0.629	1.72	0.45
0.762	3.27	0.27
0.853 <sup>b,c</sup>	5.19	0.15

<sup>a</sup>  $60^\circ$ , 0.010 M  $\text{Cr}(\text{ClO}_4)_3$ , 0.10 M  $\text{HClO}_4$ . <sup>b</sup> Equilibrium solution tagged. Diluting solution tagged in all other runs. <sup>c</sup> Two identical experiments except for length of time which elapsed between addition of diluting solution and elution.

### Interpretation of Results

The values of  $\bar{n}$  as a function of solvent composition show that, with respect to its first coordination shell, chromium(III) ion discriminates in favor of water over methanol in the mixed water-methanol solvents. A simple quantitative measure of this discrimination is the value of the quotient  $r(6 - \bar{n})/\bar{n}$ , which is the

(13) In many early experiments of this type, appreciable aquation of methanol-pentaquochromium(III) ion occurred during the elution process, which lasted prolonged periods of time (24–100 hr.). Although aquation occurred during elution in these experiments, the specific activity of early eluent portions was relatively constant; this led to the belief that values of  $\alpha_0$  calculated from such data were valid. Some of these incorrect values of  $\alpha_0$  were published. (E. L. King, J. C. Jayne, and K. Schug, Proceedings of the Seventh International Conference on Coordination Chemistry, 1962, p. 245.)

ratio of the relative amount of methanol in the solvent ( $r$ ) to the relative amount of methanol in the first coordination shell around chromium(III) ion ( $\bar{n}/(6 - \bar{n})$ ). The data of Table I give values of this quotient ranging from  $\sim 6$  at low methanol content to  $\sim 40$  at high methanol content; the discrimination in favor of water is greater the higher the methanol content of the solvent.

Of more interest than values of this ratio are values of the equilibrium constants for the stepwise reactions in which methanol molecules replace water molecules. The relationship between  $\bar{n}$  and the equilibrium constants

$$K_j = \frac{[\text{Cr}(\text{OH}_2)_{6-j}(\text{OHMe})_j^{3+}] f_j}{[\text{Cr}(\text{OH}_2)_{7-j}(\text{OHMe})_{j-1}^{3+}] f_{j-1}} \frac{a_{\text{H}_2\text{O}}}{a_{\text{MeOH}}} \quad (5)$$

is

$$\bar{n} = \frac{\sum_j K_1 K_2 \dots K_j (f_0/f_j) r_a^j}{1 + \sum_j K_1 K_2 \dots K_j (f_0/f_j) r_a^j} \quad (6)$$

in which  $f_j$  is the activity coefficient of the species  $\text{Cr}(\text{OH})_{6-j}(\text{OHMe})_j^{3+}$ , and  $r_a$  is the ratio of activities  $a_{\text{MeOH}}/a_{\text{H}_2\text{O}}$ . Since the charge on each solvated chromium(III) species is the same (3+), the ratio of activity coefficients ( $f_0/f_j$ ) is assumed to be unity in all solvent mixtures. (Support for this assumption is found in comparison of  $\bar{n}$  and  $\alpha_0$  data, to be discussed.) The applicable ratio of activities of the solvent components ( $r_a$ ) is that for the electrolyte-containing solutions studied. Since such values are not available, values for electrolyte-free binary solvent mixtures were used.<sup>14</sup> (The gross composition of the solvent was corrected, as already stated, for the solvent bound to chromium(III) ion and hydrogen ion.) Ratios of activity coefficients ( $f_{\text{MeOH}}/f_{\text{H}_2\text{O}}$ ) at rounded solvent compositions are (given as  $Z_{\text{MeOH}}$ ,  $30^\circ$  value,  $60^\circ$  value): 0.15, 1.43, 1.59; 0.20, 1.36, 1.52; 0.30, 1.17, 1.28; 0.40, 1.05, 1.09; 0.50, 0.94, 0.95; 0.60, 0.87, 0.85; 0.70, 0.82, 0.77; 0.80, 0.77, 0.71; 0.90, 0.73, 0.66; and 0.95, 0.71, 0.58. Sets of equilibrium constants have been obtained by two methods, a graphical procedure<sup>15</sup> and a high-speed computer program<sup>16</sup> for least-squares fit based on correlation of  $\bar{n}$  data suggested by Fronaeus.<sup>17</sup> The equilibrium constants so derived are presented in Table IV.

For the data at each temperature, the correlation of observed and calculated values of  $\bar{n}$  is better if one more parameter is used. This is expected, but the influence of the number of parameters used upon values of the parameters corresponding to higher values of  $j$  is disconcerting. Omitting a term corresponding to a

(14) The quality of literature values of activities of water and methanol in binary mixtures was judged by their conformity to the Gibbs-Duhem equation using procedures of E. A. Coulson and E. F. G. Herington, *Trans. Faraday Soc.*, **44**, 629 (1948), and O. Redlich and A. T. Kister, *Ind. Eng. Chem.*, **40**, 345 (1948). The data of N. M. Baron and K. P. Mishchenko, *Zh. Obshch. Khim.*, **18**, 2067 (1948), for  $25^\circ$  and of J. B. Ferguson and W. S. Funnell, *J. Phys. Chem.*, **33**, 1 (1929), for  $39.9^\circ$  were acceptable. Interpolation gave values of  $r_a$  for  $30^\circ$ . The partial pressure data by M. Wrewsky, *Z. physik. Chem.*, **81**, 1 (1912), for  $59.44^\circ$  and M. Dulitskaya, *Zh. Obshch. Khim.*, **15**, 9 (1945), for  $62.5^\circ$  were not acceptable by this criterion. The total pressure data of these independent studies, were, however, in agreement with one another after correction to  $60^\circ$ . The method of C. G. Boissonnas, *Helv. Chim. Acta*, **22**, 541 (1939), then was used to obtain partial pressure values from the total pressure data.

(15) E. L. King and P. K. Gallagher, *J. Phys. Chem.*, **63**, 1073 (1959).

(16) These calculations were performed by J. C. Sullivan of the Argonne National Laboratory.

(17) S. Fronaeus, *Acta Chem. Scand.*, **4**, 72 (1950).

species present to an appreciable extent (*e.g.*, the  $K_5$  term corresponding to  $\text{Cr}(\text{OH}_2)(\text{OHMe})_5^{3+}$  at high  $Z_{\text{MeOH}}$  at  $60^\circ$ ) distorts the equilibrium constant for

TABLE IV  
EQUILIBRIUM CONSTANTS FOR REACTIONS  
 $\text{Cr}(\text{OH}_2)_{7-j}(\text{OHMe})_{j-1}^{3+} + \text{MeOH} =$   
 $\text{Cr}(\text{OH}_2)_{6-j}(\text{OHMe})_j^{3+} + \text{H}_2\text{O}$   
 $j = 1, 2, \dots$

Reaction	-30°		-60°	
	Graphical	L. s. <sup>a</sup>	Graphical	L. s.
1	0.58	0.65	0.57	0.58
2	0.32	0.22	0.38	0.38
3	0.03	0.05	0.05	0.037
4	(0.02) <sup>b</sup>		(0.02) <sup>b,c</sup>	0.063
Av. % difference <sup>d</sup>	2.4	3.6	2.4	2.4

<sup>a</sup> In fitting data at  $30^\circ$  using the least-squares procedure, only three powers of  $r_a$  were used since the maximum observed  $\bar{n}$  value was 2.46. <sup>b</sup> Very uncertain value. <sup>c</sup> In graphical treatment of  $60^\circ$  data, allowance for  $\text{Cr}(\text{OH}_2)(\text{OHMe})_5^{3+}$  was made with  $K_5/K_4 = 8/15$ . <sup>d</sup> This is the average of the percentage difference between observed values of  $\bar{n}$  and values calculated using the set of  $K$  values given.

the next reaction (*i.e.*,  $K_4$ ). However, inclusion of a term corresponding to a species of marginal importance in a least-square treatment probably makes the corresponding parameter more important than it really should be. This is the recurring dilemma in fitting a power series to data of moderate quality taken over a limited concentration range.

The dependence of  $\alpha_0$ , the fraction of chromium(III) present as hexaaquochromium(III) ion, upon the solvent composition is obtained by combining eq. 2 and 5, which gives

$$\alpha_0^{-1} = 1 + \Sigma K_1 K_2 \dots K_j (f_0/f_j) r_a^j \quad (7)$$

Since there are fewer  $\alpha_0$  data than  $\bar{n}$  data, the  $\alpha_0$  data have not been used in an independent evaluation of the equilibrium constants, but their consistency with the  $\bar{n}$  data has been checked. If the assumption is valid that ratios of activity coefficients of the differently solvated chromium(III) ions are independent of solvent composition,  $\alpha_0$  and  $\bar{n}$  are related<sup>17</sup>

$$-\ln \alpha_0 = \int_0^{r_a} \bar{n} d \ln r_a \quad (8)$$

This integration was carried out in the machine calculation of equilibrium constants. Interpolation at values of  $r$  corresponding to the  $\alpha_0$  experiments reported in Table III gives calculated  $\alpha_0$  values (given as  $r_a, \alpha_0$ ): 0.322, 0.83; 0.825, 0.61; 1.07, 0.53; 1.42, 0.43; 2.39, 0.26; and 3.60, 0.16. (These values of  $r_a$  are those corresponding to the experimental values of  $r$ .) Agreement with experimental values of  $\alpha_0$  is within experimental uncertainty. This lends support to the assumption that the ratio of activity coefficients ( $f_0/f_j$ ) is not a function of solvent composition for  $Z_{\text{MeOH}} < 0.85$  since the differential form of eq. 8 is

$$-\frac{d \ln \alpha_0}{d \ln r_a} = \bar{n} + \frac{\Sigma K_1 K_2 \dots K_j r_a^j d(f_0/f_j)/d \ln r_a}{\Sigma K_1 K_2 \dots K_j r_a^j (f_0/f_j)} \quad (9)$$

if  $d(f_0/f_j)/d \ln r_a \neq 0$ . It must be noted, however, that the value of  $\bar{n}$  corresponding to the lowest observed value of  $\alpha_0$  is  $\sim 1.5$ . The values of  $\bar{n}$  relevant to establishment of  $K_n$  for  $n \geq 3$  have not been checked, therefore, by  $\alpha_0$ -type experiments.

In interpretation of  $\bar{n}$  data in terms of stepwise replacement of water by methanol, it has been assumed that the acid dissociation of the solvated chromium(III) is negligible. Relevant comparisons in Table I of  $\bar{n}$  data obtained at different acidities do not reveal an appreciable dependence, which means either that acid dissociation of each of the differently solvated chromium(III) ions is inappreciable in the solvents studied, or if appreciable that the extent of acid dissociation is approximately the same for each chromium(III) species.

## Discussion

The qualitative conclusion that chromium(III) ion is preferentially solvated by water in water-methanol solutions is expected on the basis of simple electrostatic theories of ion solvation by a structureless binary solvent.<sup>18</sup> In this respect chromium(III) ion is similar to europium(III) ion, the spectrum of which in aqueous methanol is unaffected by the addition of methanol until the solution is 85 mole % methanol.<sup>19</sup> (In pure methanol, the spectrum of europium(III) is different from that in water.) However, the qualitative predictions of the simple electrostatic theory fail for some systems, presumably because of the relevance of the molecular nature of the solvent. Grunwald and associates<sup>20</sup> conclude that many cations including hydrogen ion are preferentially solvated by dioxane in water-dioxane solution with  $Z_{\text{H}_2\text{O}} = 0.83$ . (In this solvent, the preferential solvation of anions by water generally more than offsets the opposite tendency of cations, and most electrolytes have a salting-out effect upon dioxane.)

Before the empirical equilibrium constants for reactions involving stepwise replacement of water by methanol (values of which are given in Table IV) are examined for their significance, a statistical correction should be applied.<sup>21</sup> Statistical correction of  $K_1$  is unambiguous and is accomplished by multiplication by  $1/6$ ; deviation of the resultant value  $K_1(\text{cor.}) = 0.10$  from unity is a quantitative measure of the discrimination of chromium(III) ion for water over methanol at this first step of methanol association. Statistical correction of  $K_2, K_3$ , and  $K_4$  is not completely straightforward because of the possible existence of isomers of species containing two, three, and four methanol molecules. If *cis* and *trans* isomers of these species are present in statistically expected relative amounts, the corrected value of  $K_j$  is obtained by multiplication of the empirical value of  $K_j$  by  $j/(7-j)$ . The values for  $60^\circ$ , so corrected, are 0.15 and 0.03 for  $j = 2$  and 3. If the assumption upon which these corrected values were obtained, that the six sites are equivalent, were valid, the corrected values would be equal to one another. They are not; therefore, the assumption is not valid. One concludes that the sites are not equivalent once the first step of methanol association is passed. The corrected values of  $K_2$  and  $K_3$  are meaningful only to the extent they disclose qualitative variation in the discrimination which chromium(III) exhibits toward

(18) (a) P. Debye, *Z. physik. Chem.*, **130**, 56 (1927); (b) G. Scatchard, *J. Chem. Phys.*, **9**, 34 (1941).

(19) E. V. Sayre, D. G. Miller and S. Freed, *ibid.*, **26**, 109 (1957).

(20) E. Grunwald, G. Baughman, and G. Kohnstam, *J. Am. Chem. Soc.*, **82**, 5801 (1960).

(21) S. W. Benson, *ibid.*, **80**, 5151 (1958).

water as the composition of its inner-solvation shell varies.

The same point is disclosed, of course, in variation of the quantity  $\bar{n}/(6 - \bar{n})r_a$  with solvent composition. Considering the data at 60°, this quantity has a value of 0.101 at  $r_a = 0.288$  (the first experimental point), a maximum value of 0.115 at  $r_a = 1.15$ , gradually decreasing to a value of 0.040 at  $r_a = 38.0$  (the last experimental point). With the ratio of activities of the solvent components as the relevant parameter, only a threefold variation in the discrimination toward water is exhibited by chromium(III). (As has already been pointed out, the variation is greater if the ratio of mole fractions is used.) A threefold variation is not large, being equivalent to only 0.73 kcal. mole<sup>-1</sup>, and extensive speculation regarding the cause of this small trend is unwarranted. The decreasing tendency for chromium(III) to bind methanol as more methanol molecules are bound may be due to a steric repulsion of methanol molecules being *cis* to one another. The dimethanol species could be exclusively the *trans* isomer, thereby eliminating *cis* methanol-methanol interactions. However, such an assignment of configuration to the dimethanol species would make  $K_2$  (cor.) = 0.76. Although this value is appreciably larger than  $K_1$  (cor.), the corresponding difference in

value of  $\Delta F^\circ$  is only  $\sim 1.3$  kcal. mole<sup>-1</sup>, which could arise from mild differences of intramolecular interactions of ligands in the species and/or solvation energies of the species with  $j = 0, 1, \text{ or } 2$ .

Although the  $\bar{n}$  values may be slightly larger at 60°, the values of  $K_1$  at 60 and 30° are within experimental error of one another and, therefore,  $\Delta H_1 = 0 \pm 0.5$  kcal. mole<sup>-1</sup> and  $\Delta S_1^\circ = -1.0 \pm 2$  cal. mole<sup>-1</sup> deg.<sup>-1</sup>. The standard states chosen and the assumptions regarding activities of solvent components and ratios of activities coefficients of solvated chromium(III) ions makes this figure correspond to

$$\begin{aligned} & (\bar{S}^\circ_{\text{Cr}(\text{OH})_2\text{OHMe}^{3+}} - \bar{S}^\circ_{\text{Cr}(\text{OH})_2\text{OH}^{3+}}) + S^\circ_{\text{H}_2\text{O}} - S^\circ_{\text{MeOH}} \\ & \text{The value of } (S^\circ_{\text{H}_2\text{O}} - S^\circ_{\text{MeOH}}) \text{ is } -13.6 \text{ cal. mole}^{-1} \\ & \text{deg.}^{-1}, \text{ giving, therefore} \\ & \bar{S}^\circ_{\text{Cr}(\text{OH})_2\text{OHMe}^{3+}} - \bar{S}^\circ_{\text{Cr}(\text{OH})_2\text{OH}^{3+}} = \\ & \qquad \qquad \qquad +14 \pm 2 \text{ cal. mole}^{-1} \text{ deg.}^{-1} \end{aligned}$$

Of this 14 cal. mole<sup>-1</sup> deg.<sup>-1</sup>, 3.6 cal. mole<sup>-1</sup> deg.<sup>-1</sup> ( $R \ln 6$ ) is due to the lower symmetry of methanolphenta-aquochromium(III) ion relative to that of hexaquo-chromium(III) ion, and the remainder is due to unresolved contributions from differences of entropies of the two gaseous ions and differences of their entropies of solution.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, NORTHWESTERN UNIVERSITY, EVANSTON, ILLINOIS]

## Carbon Monoxide Insertion Reactions. The Reaction of Methylmanganese Pentacarbonyl with Amines and Phosphines

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$\text{CH}_3\text{Mn}(\text{CO})_5$  was found to react with cyclohexylamine in ethers and in nitromethane to give  $\text{CH}_3\text{COMn}(\text{CO})_4(\text{amine})$  at a rate which was first order in  $\text{CH}_3\text{Mn}(\text{CO})_5$  but independent of the amine concentration. In methanol the rate was dependent on amine concentration but approached a limiting value at high concentrations. Similar results were obtained with triphenylphosphine and triphenyl phosphite. The reaction between  $\text{CH}_3\text{Mn}(\text{CO})_5$  and N-methylcyclohexylamine in tetrahydrofuran did not go to completion, but the rate of approach to equilibrium was first order in  $\text{CH}_3\text{Mn}(\text{CO})_5$ . In *n*-hexane the reaction between  $\text{CH}_3\text{Mn}(\text{CO})_5$  and cyclohexylamine was first order in both reactants. In mesitylene both a first-order path and a second-order path operated simultaneously. The results can all be explained by a unified mechanism involving the solvent-assisted dissociation common for nearly all octahedral complexes. Only when the coordinating ability of the solvent becomes extremely low does the nucleophilic reagent take over its role.

### Introduction

Methylmanganese pentacarbonyl reacts with a variety of nucleophiles, L, to give products of the type  $\text{CH}_3\text{COMn}(\text{CO})_4\text{L}$ . Nucleophiles known to cause this reaction include carbon monoxide,<sup>1</sup> cyclohexylamine, N-methylcyclohexylamine, aniline, and ammonia.<sup>2</sup>

It has been shown<sup>3</sup> that in the reaction with carbon monoxide, the entering molecule of carbon monoxide is not found in the acetyl group of the product.

This latter reaction has been shown<sup>4</sup> to be first order in  $\text{CH}_3\text{Mn}(\text{CO})_5$  and (in the range of carbon monoxide concentrations studied, which was severely limited by the solubility of the gas in the solvents used) first order

in carbon monoxide. The mechanism proposed by these authors for this reaction involved a direct attack on the  $\text{CH}_3\text{Mn}(\text{CO})_5$  by CO, simultaneous with an intramolecular rearrangement to form the acetyl group.

We wished to discover whether this mechanism was general for the reactions of  $\text{CH}_3\text{Mn}(\text{CO})_5$  with other nucleophiles, where the concentration range for the nucleophile was not so restricted as it is for carbon monoxide. The nucleophiles used were cyclohexylamine, N-methylcyclohexylamine, triphenylphosphine, triphenyl phosphite, and triphenylarsine.

It should be noted at this point that the stereochemistry of the complexes  $\text{CH}_3\text{COMn}(\text{CO})_4\text{L}$  was not known at the start of this work, nor did we discover any really definite evidence as to whether the incoming ligand was *cis* or *trans* with respect to the acetyl group. We have, however, recently been informed<sup>5</sup> that both isomers of the compound  $\text{CH}_3\text{COMn}(\text{CO})_4\text{P}(\text{C}_6\text{H}_5)_3$

(1) T. H. Coffield, R. D. Closson, and J. Kozikowski, *J. Org. Chem.*, **22**, 598 (1957).

(2) K. A. Kebly and A. H. Filbey, *J. Am. Chem. Soc.*, **82**, 4204 (1960).

(3) T. H. Coffield, *et al.*, Abstracts of Conference Papers, International Conference on Coordination Chemistry, London, April 6-11, 1959, Paper No. 26.

(4) F. Calderazzo and F. A. Cotton, *Inorg. Chem.*, **1**, 30 (1962).

(5) C. S. Kraihanzel, private communication.