Clausius–Clapeyron plots was obtained over the range of 105–140 °C in helium and 105–150 °C in helium containing H(tfa) vapor. As previously pointed out,[4d] above 150 °C $Mn(tfa)_3$ is gradually reduced to $Mn(tfa)_2$ in helium containing H(tfa) vapor and the decomposition of $Mn(tfa)_3$ is accelerated in the presence of $Mn(tfa)_2$. $Co(tfa)_3$ is an inert complex and thermally stable below the melting point, but above the temperature it was difficult to determine the accurate evaporation enthalpy because the deviation of vapor pressure became large in helium. $Zr(tfa)_4$ and $Hf(tfa)_4$ have about the same vapor pressures in helium and helium containing H(tfa) vapor, but there is suspicion of some thermal decomposition in helium because the chelates condensed from the vapor phase were colored yellow, while in helium containing H(tfa) vapor these chelates were recovered as white original samples. $Er(tfa)_3$, $Tm(tfa)_3$, and $Yb(tfa)_3$ were accompanied with thermal decomposition above 180 °C even in helium containing H(tfa) vapor because the lines of the Clausius–Clapeyron plots were curved.

Registry No. $Al(tfa)_3$, 14354-59-7; $Sc(tfa)_3$, 14634-68-5; $V(tfa)_3$, 15695-88-2; $VO(tfa)_2$, 14871-96-6; $Cr(tfa)_3$, 14592-89-3; $Mn(tfa)_3$, 14526-24-0; $Fe(tfa)_3$, 14526-22-8; $Co(tfa)_3$, 16827-64-8; $Co(tfa)_2$, 47115-08-2; $Ni(tfa)_2$, 14324-83-5; $Cu(tfa)_2$, 14324-82-4; $Zn(tfa)_2$, 16038-29-2; $Ga(tfa)_2$, 15453-83-5; Zr(tfa), 17499-68-2; $Pd(tfa)_2$, 63742-52-9; $In(tfa)_3$, 15453-87-9; $Er(tfa)_3$, 67118-77-8; $Tm(tfa)_3$, 97011-37-5; $Yb(tfa)_3$, 97042-23-4; $Lu(tfa)_3$, 78683-50-8; $Hf(tfa)_3$, 17475-68-2; He, 7440-59-7.

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Notes

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Chelation and Oligomerization in an Organochromium(III) System

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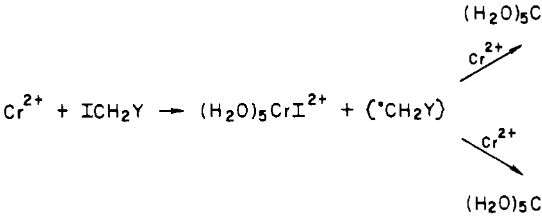
The reaction of chromium(II) and iodoacetic acid was studied by Sevcik and Jakubcova,[1] and the results reported indicate that the reaction follows the expected course, represented by the equation

$$2Cr^{2+} + ICH_2CO_2H \rightarrow (H_2O)_5CrI^{2+} + (H_2O)_5CrCH_2CO_2H^{2+} \quad (1)$$

However some $(H_2O)_5CrO_2CCH_3{}^{2+}$ should form in reaction 1 on the basis of studies of ICH_2CN,[2] ICH_2CONH_2,[3] and Cl_2CHCO_2H.[4] This prediction is based on the general mechanism



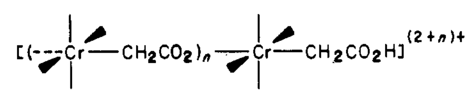
$$Cr^{2+} + ICH_2Y \rightarrow (H_2O)_5CrI^{2+} + (^{\bullet}CH_2Y) \begin{cases} \xrightarrow{Cr^{2+}} (H_2O)_5CrYCH_3 \\ \xrightarrow{Cr^{2+}} (H_2O)_5CrCH_2Y \end{cases} \quad (2)$$

The results reported here show that this expectation is correct and, of perhaps more general importance, that the organochromium(III) product has several unusual properties not consistent with its formulation in eq 1.

The first unusual property of the organochromium species formed by reaction 1 was noted during ion-exchange separation experiments. The reaction solution, which contained 0.15 M $Cr(ClO_4)_2$ and 0.105 M ICH_2CO_2H in 0.75 M $HClO_4$, was allowed to react for 10 min at 22 °C before being chromatographed at 5 °C on a 20 × 2.5 cm diameter column of Dowex 50W-X2 (H^+) (100–200 mesh). As elution proceeds with the concentration of $HClO_4$ increasing from 0.20 to 2.0 M, the products seem to elute normally with green $(H_2O)_5CrI^{2+}$ followed by a red-brown band (typical color of organochromium(III) species) and then some $Cr(OH_2)_6{}^{3+}$ (from aquation of $(H_2O)_5CrI^{2+}$). Unexpectedly, a substantial amount of red-brown species remained on the ion-exchange resin. Furthermore, when the first red-brown band was again ion exchanged on Dowex 50W-X8 (H^+)[5] almost all of the red-brown product remained on the resin even on treatment with 2 M $HClO_4$. This was unexpected because the species originally had been removed easily from Dowex 50W-X2 with 0.5 M $HClO_4$.

The separation on Dowex 50W-X8 was partially successful in that the initial red-brown eluent in 0.5 M $HClO_4$ was followed closely by a blue band. The electronic spectrum confirmed that this blue species was $(H_2O)_5CrO_2CCH_3{}^{2+}$.[6] At this stage it might be argued that this blue product is a result of the transformation which made the red-brown material so difficult to elute. However results described below show that $(H_2O)_5CrO_2CCH_3{}^{2+}$ is a product of the initial reaction.

The ion-exchange behavior can be explained by oligomerization occurring on the ion-exchange resin. The system appears to take advantage of the high local concentrations on the resin and the lability of the trans water molecule[7] in organopentaaquochromium(III) species to condense to give polymeric species, e.g.



The greater extent of the reaction (larger *n*) on X8 compared to X2 resin may be attributed to the greater density of anionic sites on the former, giving a greater concentration of the adsorbed cation.

The conclusion that the oligomerization occurs on the resin is substantiated by the observation that a solution of the red-brown eluent in 0.50 M $HClO_4$ shows no spectrophotometric change on storage at 5 °C for 24 h or at 25 °C for 30 min.

The behavior of the organochromium species on the ion-exchange column complicates a study of the true products of reaction 1. However a detailed analysis of the electronic spectra of various fractions eluted from Dowex 50W-X2 (H^+) at 5 °C shows that the products are not just $(H_2O)_5CrI^{2+}$ and $(H_2O)_5CrCH_2CO_2H^{2+}$.

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[5] The higher cross-linking was chosen to better separate $(H_2O)_5CrO_2CCH_3{}^{2+}$ and $(H_2O)_5CrCH_2CO_2H^{2+}$.

[6] Deutsch, E.; Taube, H. *Inorg. Chem.* **1968**, *7*, 1532. The absorption maxima (and extinction coefficients) of $(H_2O)_5CrO_2CCH_3{}^{2+}$ are reported as 570 nm (24.4 M^{-1} cm^{-1}) and 410 nm (22.2 M^{-1} cm^{-1}).

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Table I. Electronic Spectra of Red-Brown Fractions from Ion Exchange of Cr^{2+} + ICH_2CO_2H Reaction Products[a]

fraction				
[eluent],[b] M	vol,[c] mL	abs max, nm (ϵ,[d] $M^{-1}\ cm^{-1}$)		
0.5	0–10	548 (30.4)	414.5 (69.2)	271 (2.50×10^3)
0.5	10–20	552 (27.1)	414 (58.9)	272 (1.91×10^3)
0.5	20–80	554 (25.7)	413 (50.5)	270.5 (1.52×10^3)
0.5	80–120	551 (27.3)	412 (55.3)	270.5 (1.74×10^3)
3–4	200–300	524 (48.8)	408 (74.5)	271 (2.84×10^3)

[a] The initial reaction solution contained 0.15 M Cr^{2+} and 0.105 M ICH_2CO_2H in 0.75 M $HClO_4$. [b] Eluent is $HClO_4$ in all cases. [c] Volume of fraction collected at flow rate of ~10 mL min^{-1}. [d] Extinction coefficients are based on total chromium determined by oxidation to chromate with H_2O_2. Since all were measured under the same conditions in the same cells, the relative uncertainty between values is ≤1%.

The results, summarized in Table I, give the properties of various red-brown fractions of the fraction initially eluted from X2 in 0.5 M $HClO_4$. The longest wavelength peak shifts from 548 to 554 nm for the first three fractions, while the extinction coefficients decrease in the 550- and 270-nm regions. The fourth fraction reverses this trend, and the final fraction in 3–4 M $HClO_4$ shows a substantial blue shift to 524 nm, and an increase in extinction coefficients at all absorption maxima.

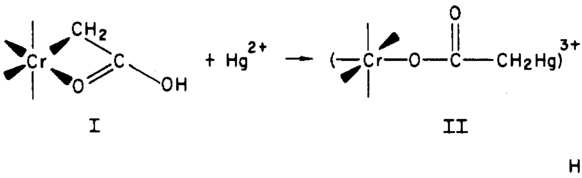
The results in Table I can be explained if the red-brown band is actually a mixture of $(H_2O)_5CrCH_2CO_2H^{2+}$ and $(H_2O)_5CrO_2CCH_3^{2+}$, which are not fully separated by the rather rapid ion-exchange conditions necessary to combat the oligomerization reaction discussed above. The relative amount of $(H_2O)_5CrO_2CCH_3^{2+}$ must increase from fractions 1 through 3 to explain the changes in position of the absorption maxima and apparent extinction coefficients.[6] The fourth fraction probably contains some oligomer (e.g. $n = 1$, charge = 3+), and the final fraction in 3–4 M $HClO_4$ contains higher oligomers.

A further peculiarity of the organochromium(III) product is shown by its reaction with mercury(II). This reaction normally proceeds as[7]

$$(H_2O)_5CrCH_2R + Hg^{2+} \xrightarrow{H_2O} Cr(OH_2)_6^{3+} + HgCH_2R^+ \quad (3)$$

When a portion of the third fraction in Table I was mixed with excess $Hg(ClO_4)_2$ in 0.5 M $HClO_4$ (Hg(II):Cr(III) = 2:1), the solution quickly changed from red-brown to green, but no $Cr(OH_2)_6^{3+}$ was detected after ion-exchange separation. Only two species were separated. A blue species is easily eluted from Dowex 50W-X2 with 0.5 M $HClO_4$, and its absorption maxima, 571 and 411 nm, and extinction coefficients, 25.0 and 23.8 $M^{-1}\ cm^{-1}$, respectively, indicate that it is $(H_2O)_5CrO_2CCH_3^{2+}$.[6] This species is present as a product of the initial reaction of Cr(II) and ICH_2CO_2H. The second product eluted with 2 M $HClO_4$ is blue also with absorption maxima at 571 and 409 nm and extinction coefficients of 20.8 and 20.9 $M^{-1}\ cm^{-1}$, respectively. This second product contains 39.5% of the total chromium(III) in the original third fraction,[8] and it contains mercury as shown by reaction with Cu metal.

The original organochromium species must be formulated to explain the facts that the reaction with mercury(II) yields no $Cr(OH_2)_6^{3+}$ and that the reaction product contains both Cr(III) and Hg(II). This behavior is consistent if the original species is a chelate (I). Then the reaction proceeds according to eq 4. The electronic spectrum of II is similar to that of $(H_2O)_5CrO_2CCH_3^{2+}$, as expected. The protonated form of I seems to be required by the similarity in charge of I and $(H_2O)_5CrO_2CCH_3^{2+}$ as implied by the difficulty in separating the two species by ion-exchange chromatography. Since the spectrum of I is unchanged in 0.10 and 0.50 M $HClO_4$, it must have a K_a < 0.1 M.



(4)

From the knowledge gained about the reactivity of the organochromium(III) species (I), it is possible to design a convenient experiment to determine the amount of $(H_2O)_5CrO_2CCH_3^{2+}$ formed from Cr^{2+} + ICH_2CO_2H. When the reaction is complete, excess $Hg(ClO_4)_2$ can be added to catalyze aquation of $(H_2O)_5CrI^{2+}$ and to convert I to II. Then the solution will contain $(H_2O)_5CrO_2CCH_3^{2+}$, $Cr(OH_2)_6^{3+}$, and $(H_2O)_5CrO_2CCH_2Hg^{3+}$, and the first species can be separated easily from the others to determine the amount formed. When 0.15 M Cr^{2+} reacts with 0.15 M ICH_2CO_2H in 0.50 M $HClO_4$, 81% of the ICH_2CO_2H reacting appears as $(H_2O)_5CrO_2CCH_3^{2+}$ in the product.

The results reported here provide a basis for reassessing the results of numerous studies[7] on the chromium(II) reduction of various organic carboxylic acids. These observations provide an important basis for predicting the prescence of oligomerization reactions and chelated species in organochromium systems.

Experimental Section

Chromium(II) perchlorate (~0.5 M in 0.10 M $HClO_4$) was prepared by reducing chromium(III) perchlorate with amalgamated zinc under argon. Sodium iodoacetate (Fisher) was used as supplied. The $Hg(ClO_4)_2$ solutions were prepared by dissolving HgO (yellow) (Anachemia) in excess perchloric acid. Low-temperature ion exchange was done in a cold room at +5 °C. The electonic spectra were recorded on a Cary 219 spectrophotometer. Standard methods of handling and analysis are described elsewhere.[2]

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Registry No. $Cr(ClO_4)_2$, 13931-95-8; ICH_2CO_2H, 64-69-7; $(H_2O)_5CrI^{2+}$, 18955-06-1; $Cr(OH_2)_6^{3+}$, 14873-01-9; $(H_2O)_5CrO_2CCH_3^{2+}$, 18894-45-6; $(H_2O)_5CrCH_2CO_2H^{2+}$, 52032-35-6; $(H_2O)_5CrO_2CCH_2Hg^{3+}$, 96807-98-6.

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[8] If the 39.5% represents the amount of organochromium species in the third fraction, and 60.5% is $(H_2O)_5CrO_2CCH_3^{2+}$, then the known spectrum of the latter[6] can be used to calculate the extinction coefficients of the organochromium species at 554, 413, and 270 nm as 26, 69, and 2.5×10^3 $M^{-1}\ cm^{-1}$, respectively.

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Theoretical Study of the Electronic Structure and Bonding in $Ni(PF_3)_4$

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Although formerly subject to controversy, it is now generally considered that substituted phosphines are capable of important π-acceptor behavior.[1] However, the extent of the π bonding depends strongly on the nature of the groups attached to the phosphorus atom, particularly on the electronegativity and the size of these groups. For a long time now, chemists have realized that the ligand PF_3 is quite similar to CO[2] in both its σ-donor and π-acceptor characteristics. Experimental evidence from IR,[3]

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(1) See, for instance: "Transition Metal Complexes of Phosphorus, Arsenic and Antimony Ligands"; McAuliffe, C.A., Ed.; Macmillan: London, 1973. McAuliffe, C. A.; Levason, W. "Phosphine, Arsine and Stibine Complexes of the Transition Elements"; Elsevier: Amsterdam, 1979. Booth, G. *Adv. Inorg. Chem. Radiochem.* **1964**, *6*, 1–69. Emsley, J.; Hall, D. "The Chemistry of Phosphorus"; Wiley: New York, 1976.

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