Even after several hours no evidence of formation of hexane was obtained.

By reaction of hydrogen chloride with *trans*-$Pt(P(C_2H_5)_3)_2HCl$ in dichloroethane the formation of the dihydride in the solution was monitored by following the appearance of an infrared band at 2252 cm^{-1} assigned to ν(Pt–H) [ν(Pt–H) in Nujol at 2254 cm^{-1} [4]]. Reduction of 1-hexene to hexane did not occur in dichloroethane.

Kinetics.—Fresh 99.5% ethanol solutions of $Pt(P(C_2H_5)_3)_2HCl$ only and 1-hexene containing mineral acid HA (HCl or $HClO_4$) were prepared and stored separately in a thermostat. The reaction was started by mixing known volumes of the two solutions in a 1-cm quartz cell placed in a thermostated (30°) cell compartment of a Beckman DK-2A recording spectrophotometer. The reaction was followed by scanning the spectra in the ultraviolet region from time to time. All runs were carried out under pseudo-first-order conditions by changing alternatively the concentration of olefin, acid, and chloride ion, the initial concentration of complex being kept constant. The dependence of the pseudo-first-order rate constants k_{obsd} (sec^{-1}) on the concentrations of Cl^-, H^+, and olefin was investigated. The k_{obsd} values were determined as usual from the slopes of the plots of log ($A_\infty - A_t$) *vs.* time.

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Kinetic Studies on the 1:1 Complex of Iron(III) and Chromate Ions in Perchloric Acid Solution[1a]

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Rate studies have been carried out on the complex formation reaction of Fe^{3+} and $HCrO_4^-$. The rate expression is $d[FeCrO_4^+]/dt = k_f[Fe^{3+}][HCrO_4^-][H^+]^{-1} - k_a[FeCrO_4^+]$ with $k_f = 35.0 \pm 1.3$ sec^{-1} and $k_a = 15.1 \pm 1.3$ sec^{-1} at 25.0° and 1.00 *M* ionic strength ($LiClO_4$). The stability quotient of $FeCrO_4^+$ obtained from the rate studies was confirmed by independent spectrophotometric measurements. The proposed mechanism involves substitution of $HCrO_4^-$ on $FeOH^{2+}$, in accord with other iron(III) substitution reactions.

Introduction

Complexes of CrO_4^{2-} with metal ions have not been studied extensively. King and Neptune[2] found the intense light absorption in solutions of Cr(III) and Cr(VI) was due to the complex $CrCrO_4^+$ whose stability, however, was too small to evaluate. Tong and King[3] have found complex formation between Ce(IV) and CrO_4^{2-} and Sullivan and French[4] studied the association of $Co(NH_3)_5(OH_2)^{3+}$ and CrO_4^{2-}, concluding that both slowly established and rapid equilibria were important, corresponding to inner and outer complexes.

In a kinetic study of the mechanisms of oxidation of Fe^{2+} by $HCrO_4^-$, Espenson and King[5] noted extensive complexing of Fe^{3+} by $HCrO_4^-$ according to

$$Fe^{3+} + HCrO_4^- = FeCrO_4^+ + H^+ \qquad (I)$$

We have carried out a study of the forward and reverse rates of reaction I under a wide variation of concentrations of Fe^{3+}, $HCrO_4^-$, and H^+ at 25.0° with lithium perchlorate added to maintain an ionic strength of 1.00 *M*.

Experimental Section

Materials.—Hydrated iron(III) perchlorate was prepared by fuming the chloride with perchloric acid, and its solutions were analyzed by accepted procedures.[6] Potassium dichromate solutions were prepared from the reagent grade solid. Lithium carbonate was used to prepare the perchlorate which was recrystallized three times. Reagent grade perchloric acid was used without further purification. All solutions were made up with conductivity water.

Procedures.—Spectrophotometric measurements were carried out using a Cary Model 14 recording spectrophotometer in which the sample temperature was maintained at 25.0 ± 0.2° by circulating water.

The rate studies were carried out using a spectrophotometric stopped-flow apparatus[6] based on the design of Dulz and Sutin.[7] The wavelength chosen was often 380 nm, λ_{max} for $FeCrO_4^+$, but frequently studies were carried out at longer wavelengths to limit the total absorbance change to 0.1.[6]

Results

Rate Experiments.—Perchloric acid was in considerable excess over the changes in concentration of the other substances, so that its concentration remained effectively constant. The rate can be represented by

$$d[FeCrO_4^+]/dt = k_f'[Fe^{3+}][HCrO_4^-] - k_a'[FeCrO_4^+] \qquad (1)$$

where k_f' and k_a' represent rate constants at any particular $[H^+]$.

In all experiments the iron(III) concentration was in considerable excess over chromium(VI) so that the integrated rate expression is that given by eq 2, with concentrations replaced by absorbances (*D*). The

$$-d \ln (D_\infty - D)/dt = k_{app} = k_a' + k_f'[Fe^{3+}] \qquad (2)$$

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(1) (a) Work performed in the Ames Laboratory of the U. S. Atomic Energy Commission. Contribution No. 2459. (b) Fellow of the Alfred P. Sloan Foundation 1968–1970. (c) Based on the M.S. thesis of S. R. H., Iowa State University, Aug 1968.

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

(3) J. Y. Tong and E. L. King, *ibid.*, **76**, 2132 (1954).

(4) J. C. Sullivan and J. E. French, *Inorg. Chem.*, **3**, 832 (1964).

(5) J. H. Espenson and E. L. King, *J. Am. Chem. Soc.*, **85**, 3328 (1963).

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

(7) G. Dulz and N. Sutin, *ibid.*, **2**, 917 (1963).

pseudo-first-order behavior predicted by eq 2 is illustrated in Figure 1 by rate plots for two typical runs, with the data treated by the method of Guggenheim[8] to avoid dependence of the rate constant on the single value measured for D_∞. Consistent with eq 2, values of the pseudo-first-order rate constant k_{app} were not dependent on the initial chromium(VI) concentration which was varied from 5×10^{-5} to 8×10^{-4} *M*. At these low Cr(VI) concentrations $Cr_2O_7^{2-}$ is not an important species,[9] and $HCrO_4^-$ predominates (≥93%). At the low acidities used, $[H^+] \leq 0.2$ *M* with most studies having ≤0.050 *M* H^+, H_2CrO_4 can also be ignored.[9] The rate constants also proved independent of the wavelength at which the formation of $FeCrO_4^+$ was followed. At each particular $[H^+]$, plots of k_{app} *vs.* $[Fe^{3+}]$ were linear within experimental error.

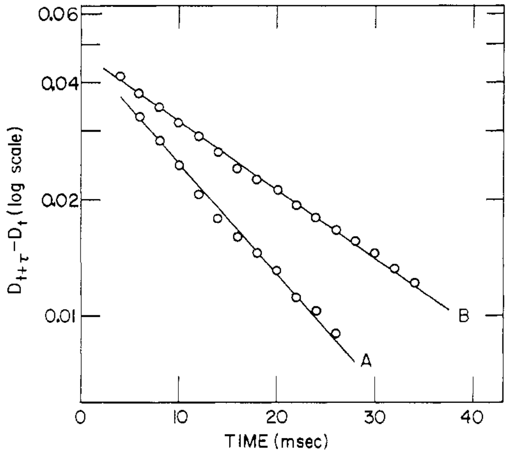

Figure 1.—Guggenheim plots of typical rate experiments: (A) 0.025 *M* H^+, 0.035 *M* Fe^{3+}, 4.0×10^{-4} *F* $HCrO_4^-$, λ 460 nm, $\Delta D = 0.060$ (optical path ~0.3 cm), $k_{app} = 65.8$ sec^{-1}; (B) 0.050 *M* H^+, 0.015 *M* Fe^{3+}, 4.0×10^{-4} *F* $HCrO_4^-$, λ 380 nm, $\Delta D = 0.060$ (optical path 0.3 cm), $k_{app} = 40.6$ sec^{-1}.

Experiments were done with $[H^+]$ varied from 0.0125 to 0.200 *M*, $LiClO_4$ being added to maintain 1.00 *M* ionic strength. The family of lines according to eq 2 had the same intercept, suggesting the rate expression

$$k_{app} = k_a + (k_f[Fe^{3+}]/[H^+]) \qquad (3)$$

where the parameters now represent "true" rate constants; that is, they are not further dependent upon concentration variables. A plot of all the data according to eq 3 is presented in Figure 2, in which a vertical error bar represents the average deviation, usually 2–10% from the mean of k_{app} at a particular combination of hydrogen ion and iron(III) concentrations. A least-squares fit of the data to eq 3 gave the values $k_a = 35.0 \pm 1.3$ sec^{-1} and $k_f = 15.1 \pm 1.3$ sec^{-1}.

Equilibrium Experiments.—One value of the equilibrium quotient for reaction I is obtained from the quotient of rate constants: $Q = k_f/k_a$. The value determined on this basis is 0.43 ± 0.05.

A spectrophotometric study similar to that published, but under different conditions,[5] was also carried out to obtain an independent value of *Q* under the same conditions as the rate measurements, 25.0° and $\mu = 1.00$ *M*. Absorbance measurements at 380 nm were made on solutions containing concentrations of 0.005–0.035 *M* Fe^{3+}, $0\text{–}4 \times 10^{-4}$ *F* Cr(VI), and 0.0125 *M* H^+. The value of *D* per unit path length at each iron(III) concentration varied linearly with [Cr(VI)] and gave the slopes 1640, 2480, 3040, and 3380 M^{-1} cm^{-1} at 0.005, 0.015, 0.025, and 0.035 *M* Fe^{3+}, respectively. Equation 4[5] describes the relation of these slopes ($\bar{\epsilon}$) to the molar absorptivity of the complex (ϵ_{36}), to that of Cr(VI) (ϵ_6), and to the equilibrium quotient.

$$\bar{\epsilon} = (\bar{\epsilon} - b\epsilon_6)\frac{[H^+]}{Q[Fe^{3+}]} + b\epsilon_{36} \qquad (4)$$

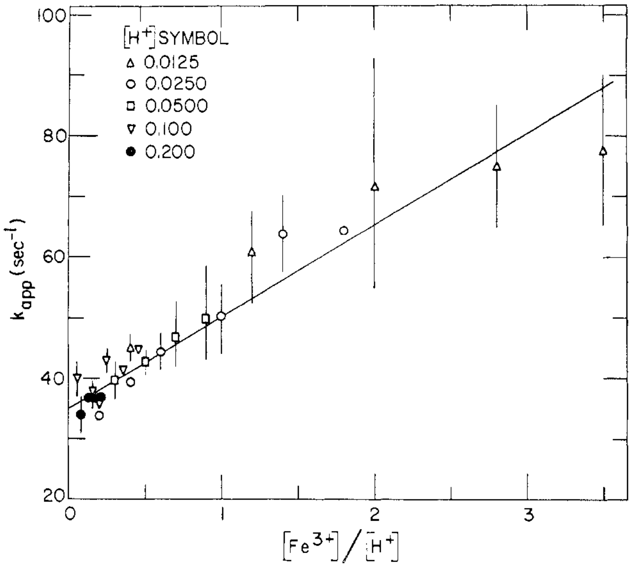

Figure 2.—A plot of k_{app} *vs.* $[Fe^{3+}]/[H^+]$, according to eq 3. Error bars represent average deviations of individual rate constants from the mean. The line is the least-squares fit.

From such a plot with $\epsilon_6 = 980$ M^{-1} cm^{-1}, *Q* was 0.45 and ϵ_{36} was 5.3×10^3 M^{-1} cm^{-1} as shown in Figure 3. The values of *Q* proved quite sensitive to the values of $\bar{\epsilon}$ taken from the slopes of *D* *vs.* [Cr(VI)], however, and the good agreement with the rate experiments may be fortuitous. The spectrophotometric value has associated with it an uncertainty of probably 20%. The present value $Q = 0.43 \pm 0.05$ at 25.0° and $\mu = 1.00$ *M* can be compared to $Q = 1.4$ at 0° and $\mu = 0.084$ *M* obtained in the earlier studies.[5]

Interpretation and Discussion

The rate expression for reaction I written in terms of the predominant species of reactants and products is given by

$$d[FeCrO_4^+]/dt = (k_f[Fe^{3+}][HCrO_4^-]/[H^+]) - k_a[FeCrO_4^+] \qquad (5)$$

suggesting either of two plausible mechanisms: mechanism A

$$HCrO_4^- \overset{K_{Cr}}{=} H^+ + CrO_4^{2-} \qquad (II)$$

$$Fe(H_2O)_6^{3+} + CrO_4^{2-} \overset{K_{ip}}{=} \text{ion pair} \underset{k_2}{\overset{k_1}{\rightleftarrows}} Fe(H_2O)_5OCrO_3^+ + H_2O \qquad (III)$$

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[8] E. A. Guggenheim, *Phil. Mag.*, [7] **2**, 538 (1926).

[9] J. Y. Tong and E. L. King, *J. Am. Chem. Soc.*, **75**, 6180 (1953).

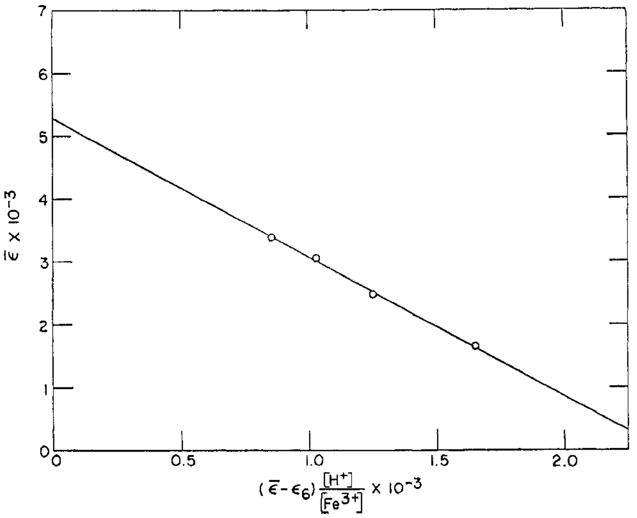

Figure 3.—Equilibrium studies on $FeCrO_4^+$ plotted in accord with eq 4.

or mechanism B

$$Fe(H_2O)_6^{3+} \overset{K_{Fe}}{=} Fe(H_2O)_5OH^{2+} + H^+ \qquad (IV)$$

$$Fe(H_2O)_5OH^{2+} + HCrO_4^- \overset{K'_{ip}}{=} \text{ion pair} \underset{k_4}{\overset{k_3}{\rightleftarrows}} Fe(H_2O)_5OCrO_3^+ + H_2O \qquad (V)$$

In each case the rate-determining step in forming the complex is represented as loss of water from an ion pair. According to each, the parameters are: A, $k_f = k_1K_{Cr}K_{ip}$, $k_a = k_2$; B, $k_f = k_3K_{OH}K'_{ip}$, $k_{aq} = k_4$. These kinetically indistinguishable mechanisms can perhaps be resolved by arguments similar to those advanced previously.[6,10,11]

The published values[9,12] are $K_{Cr} = 3 \times 10^{-7}$ M and $K_{Fe} = 1.65 \times 10^{-3}$ M, giving $k_1K_{ip} = 5 \times 10^7$ M^{-1} sec^{-1} and $k_3K'_{ip} = 9.2 \times 10^3$ M^{-1} sec^{-1}. The first value is substantially higher than the range of values (4–127 M^{-1} sec^{-1}) found[6,10] for substitution of neutral and monoanionic ligands on $Fe(H_2O)_6^{3+}$. Although one expects that a divalent anion, with its correspondingly higher value of K_{ip}, would thus exhibit a higher rate, 5×10^7 M^{-1} sec^{-1} appears unreasonably high considering the H_2O exchange rate constant for $Fe(H_2O)_6^{3+}$ is 280 M^{-1} sec^{-1}.[13]

The rates of the substitution reactions of $Fe(H_2O)_5OH^{2+}$ by monoanions have been found to lie in the range $(1–2.6) \times 10^4$ M^{-1} sec^{-1}, replacing the values for HSO_4^- in Seewald and Sutin's tabulation[10] by those from the recent studies of Cavasino.[14] The value computed for mechanism B agrees well with this range, whereas that for A is unreasonable. Additional support comes from the fact that in other cases where this type of proton ambiguity exists scheme B has invariably proven to be the preferable choice.[6,10]

By analogy with other iron(III) reactions a two-term rate expression had been anticipated in which the forward rate would have been

$$d[FeCrO_4^+]/dt = [Fe^{3+}][HCrO_4^-](\alpha + (k_f/[H^+]))$$

The measurements were restricted to $[H^+] \leq 0.20$ M in order that sufficient complex be present to observe. With $k_f = 15$ sec^{-1}, $k_f/[H^+]$ was 75–1200 M^{-1} sec^{-1}. Thus it did not prove surprising that $k_f/[H^+]$ so greatly exceeded α under the conditions of this study that it could not be observed, since the anticipated value of α was 4–127 M^{-1} sec^{-1} with the most likely value near the low end, as for all other complexes except the thiocyanate. We estimate the upper limit $\alpha \leq 4$ M^{-1} sec^{-1}.

The mechanism probably involves substitution at iron(III) and not at chromium(VI). In the first place, the rate constant correlates well with mechanism B on that basis. Secondly, the rate is somewhat higher than that noted for Cr(VI)–solvent exchange as noted in the study of Swinehart and Castellan[15] on the $HCrO_4^-$–$Cr_2O_7^{2-}$ interconversion. In support of this, Sullivan and French[4] noted that formation of the inner complex of $(NH_3)_5CoOH_2^{3+}$ and $HCrO_4^-$, which necessarily involved Cr(VI) substitution, required considerably longer times.

For the same reasons, the complex is not merely an ion-pair or outer-sphere complex of Fe^{3+} and CrO_4^{2-} since such an association would occur at rates very much higher than noted here. The rapidity of the Cr(III)–$HCrO_4^-$ interaction[2] suggests that ion pairs are responsible for the absorbance enhancement, for aquation of an inner complex should not occur as rapidly as reported.[2] We attempted to measure this reaction rate and found it complete upon mixing (4 msec). It is tempting to ascribe this to ion-pair formation, but it must also be noted that the observable rate as in eq 5 is a sum of aquation and formation rates. A sufficiently unstable inner complex may have k_a so large as to give a value of k_{app} beyond the range of the technique employed.

A further point with regard to the structure of the complex $FeOCrO_3^+$ is that we have assumed in reactions III and V that CrO_4^{2-} acts as a monodentate ligand. Since closing of the chelate would be expected to be fast relative to the initial substitution in view of the much higher exchange rate[13] of $FeOH^{2+}$ over Fe^{3+}, conversion of monodentate $(H_2O)_5FeOCrO_3^+$ to chelated $(H_2O)_4FeO_2CrO_2^+$ would probably not have been observed in these measurements making it impossible to rule out the chelated structure. Chelation is deemed unlikely, however, and the confirmation[16] of a monodentate SO_4^{2-} group in the complex $(H_2O)_5CrOSO_3^+$ should be noted. An additional ambiguity related to the proton arrangement is also noted and it cannot be asserted that the formula is $(H_2O)_5FeOCrO_3^+$ rather than $(H_2O)_4Fe(OH)(HCrO_4)^+$.

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

(11) M. Eigen and R. G. Wilkins, Advances in Chemistry Series, No. 49, American Chemical Society, Washington, D. C., 1965, p 48.

(12) R. M. Milburn and W. C. Vosburgh, *J. Am. Chem. Soc.*, **77**, 1352 (1955).

(13) R. E. Connick and E. D. Stover, *J. Phys. Chem.*, **65**, 2075 (1961).

(14) F. P. Cavasino, *ibid.*, **72**, 1378 (1968).

(15) J. H. Swinehart and G. W. Castellan, *Inorg. Chem.*, **3**, 278 (1964).

(16) J. E. Finholt, R. W. Anderson, J. A. Fyfe, and K. G. Caulton, *ibid.*, **4**, 43 (1965).