pounds[12] has shown that the difference between the ν_1 and ν_3 modes for the uranyl group is always in the range of 70–80 cm^{-1}. The amorphous amide $UO_2(NH_2)_2 \cdot NH_3$ is presumably polymeric, possibly containing both bridging amide and ammine groups and discrete linear uranyl groups.

The ir spectrum of the deammoniation product $UO_2NH(NH_4Br)_2$ does not show either ν(U–Br) or the presence of coordinated NH_3; the band at 891 cm^{-1} is clearly ν(U–O) and its position and shape suggests the absence of discrete linear uranyl groups in the imide.[13] Ammonium bromide may be washed from this mixture with liquid ammonia; the insoluble product is the amorphous 2-ammoniate, $UO_2NH \cdot 2NH_3$, in the absence of any ammonia-soluble uranium-containing species. This lends further evidence for the formulation given above for $[UO_2(NH_2)_2 \cdot NH_3](NH_4Br)_2$ since if the 2-ammoniate of the imide were present it should be possible to remove NH_4Br by washing. It is reported[3] that UO_2NH does not react with ammonium iodide; this also is in accordance with our observations.

It seems most likely that the $(UO_2Br_4)^{2-}$ ion is ammonolyzed in liquid ammonia to form a complex of the type $(NH_4)_2[UO_2Br_2(NH_2)_2]$ which is sparingly soluble and stable in ammonia but decomposes upon removal of the solvent to form $[UO_2(NH_2)_2 \cdot NH_3](NH_4Br)_2$. An analogous mechanism has been proposed to explain the ammonolysis of hexachlorotitanium(IV) complexes.[14]

The ir spectrum of $UO_2NH \cdot 2NH_3$ confirms the presence of coordinated ammonia and includes ν(U–O) at 877 cm^{-1}. Partial deammoniation occurs *in vacuo* at 200° to give $UO_2NH \cdot NH_3$; again there is ir evidence for coordinated ammonia and a band at 890 cm^{-1} assigned to ν(U–O). The 1-ammoniate undergoes reductive decomposition at 330° to give impure U_3O_8 probably containing minor quantities of other oxides and nitrides.

The ammoniated amide $UO_2(NH_2)_2 \cdot NH_3$ is extremely soluble in and reactive with dilute acids; hydrolysis yields $3UO_3 \cdot NH_3 \cdot 5H_2O$ which was previously isolated from the ternary system UO_3–NH_3–H_2O[15] and by addition of NH_3 to an aqueous solution of a uranyl salt.[16] These products also[6] were characterized by X-ray diffraction data.

The reaction of $[UO_2(NH_2)_2 \cdot NH_3](NH_4Br)_2$ with CH_3OH affords a convenient route to $UO_2(OCH_3)_2 \cdot CH_3OH$ previously formed from UO_2Cl_2 and $LiOCH_3$;[17,18] we report here ir data for this compound. With benzoic acid we obtained a salt $NH_4[UO_2(C_6H_5CO_2)_3]$. The crystalline product obtained from reaction with acetylacetone was identical with a compound previously obtained from uranyl nitrate and acetylacetone in the presence of NH_3.[8,19] There is considerable uncertainty about the nature of this compound; recent studies[8] employing ir and ^1H nmr data suggest that it is a β-ketoimine solvate of dioxobis(acetylacetonato)uranium(VI) and our observations are consistent with this postulate.

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Kinetic Study of the Oxidation of Ferrocene by Chromium(VI)[1a]

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The oxidation–reduction chemistry of ferrocene has received very little previous attention, although studies of Duke[2] and Stranks,[3] as well as earlier work from this group,[4] have been reported. A considerable body of work is now available concerning the kinetics and mechanism of oxidation of metal complexes by chromium(VI); these studies have been reviewed recently.[5]

In the present work we report the results of a kinetic study of the oxidation of ferrocene by Cr(VI), which occurs according to the reaction

$$3Fe(C_5H_5)_2 + HCrO_4^- + 7H^+ = 3Fe(C_5H_5)_2^+ + Cr^{3+} + 4H_2O \quad (1)$$

Experimental Section

Ferrocene from Alfa Inorganics was purified by vacuum sublimation. Potassium dichromate and perchloric acid were reagent grade chemicals used without additional purification. Lithium perchlorate was prepared from the carbonate and was twice recrystallized. Conductance water, prepared by a distillation from alkaline permanganate in a tin-lined still, was used throughout. The ferrocene stock solutions were analyzed by a spectrophotometric titration using a Fe^{3+} solution at the wavelength maximum for $Fe(C_5H_5)_2^+$, 618 nm. This reaction is known to occur with a 1:1 stoichiometry,[4b] and the ferrocene concentrations so determined were within 1% of the concentrations computed based on the weighed amount of ferrocene.

The reaction was studied in a mixed water–acetone solvent, 1:1 by volume, with the mole fraction of acetone in the solvent equal to 0.195. The reaction was studied in perchloric acid solutions with $[H^+] \geq 0.05$ *M*, and ionic strength was maintained at 1.00 *M* by addition of lithium perchlorate.

The kinetic measurements were carried out using a Durrum stopped-flow spectrophotometer equipped with a Kel-F mixing chamber having a 2-cm optical path.

A complication due to certain side reactions had to be considered. First, $HCrO_4^-$ slowly oxidizes acetone if the solution is acidic, so that solutions prepared in this manner decomposed appreciably in the time needed to begin the rate measurements. Also, solutions of ferrocene in aqueous acetone, while stable if neutral, are subject to slow decomposition if acidified. These problems were circumvented by the following procedure. The reaction between $HCrO_4^-$ and $Fe(C_5H_5)_2$, eq 1, requires acid to proceed; in neutral solution these reagents are stable together. The kinetic measurements were carried out by preparing one reservoir solution to contain both $HCrO_4^-$ and $Fe(C_5H_5)_2$, but no perchloric acid. The second solution consisted of perchloric acid, also in aqueous acetone. The reaction in eq 1 which occurs upon mixing is far more rapid than either of the other side re-

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actions; consequently, it could be studied by this mixing procedure without any interference from either the oxidation of acetone or the decomposition of ferrocene.

The kinetic experiments were carried out at four different wavelengths in the range 330–618 nm. The molar absorptivities of the species involved at the specific wave lengths studied are given in Table I. The reaction rate was independent of the wavelength used to study the reaction, indicating the probable absence of reaction intermediates which attain significant concentration.

TABLE I

WAVELENGTHS AND MOLAR ABSORPTIVITIES FOR REACTANTS AND PRODUCTS[a]

	ϵ, M^{-1} cm^{-1}			
λ, nm	$Fe(C_5H_5)_2$	$Fe(C_5H_5)_2^+$	$HCrO_4^-$	Cr^{3+}
330	53	1280	1170	8
350	19	588	1600	10
370	17	380	1260	12
618	~0	450	~0	10

[a] In water–acetone (1:1, v/v).

The reaction was studied under concentration conditions where both $[Fe(C_5H_5)_2]$ and $[H^+]$ were much larger than $[Cr(VI)]$. Pseudo-first-order plots were made based on the readings of absorbance (D) taken from the Polaroid photographs of the reaction trace displaced on the oscilloscope screen. The kinetic data were treated according to the equation

$$\ln (D_\infty - D_t) = \ln (D_\infty - D_0) - k_{obsd}t \qquad (2)$$

which resulted in a good fit for the kinetic data in every experiment. Division by the average concentration of ferrocene present in the particular run yielded the value of the apparent second-order rate constant k' appropriate to the hydrogen ion concentration in question.

Experiments with Cr(VI) in excess could not be carried out since Cr(VI) oxidizes $Fe(C_5H_5)_2^+$ with irreversible destruction of metal–ligand bonds. Under these conditions the stoichiometry is not given by eq 1. The oxidation of $Fe(C_5H_5)_2^+$ by Cr(VI) is slow compared to the oxidation of $Fe(C_5H_5)_2$ by Cr(VI) and does not represent a complication for the studies reported here with excess $Fe(C_5H_5)_2$.

The stoichiometry of the reaction, eq 1, was determined by spectrophotometric analysis at 618 nm of the ferricenium ion produced by reaction with a known amount of Cr(VI). Under concentration conditions of $[Fe(C_5H_5)_2] \geq 3[Cr(VI)]$ the reaction gave cleanly the stoichiometry expressed by eq 1.

Results and Discussion

The kinetic data from each experiment are given in Table II. At a particular $[H^+]$ the apparent second-order rate constant does not show a dependence upon $[Fe(C_5H_5)_2]$ over a 20-fold concentration variation, confirming the rate expression

TABLE II

RATE CONSTANTS FOR THE REACTION OF FERROCENE AND CHROMIUM(VI)[a]

Initial concentrations, M			
$[H^+]$	$10^5[Cr(VI)]$	$10^3[Fe(C_5H_5)_2]$	$10^2k'$, M^{-1} sec^{-1}
0.050	3.34	1.01	4.90
0.050	3.00	2.06	4.86
0.050	0.40	0.12	5.17
0.050	2.00	0.60	4.91
0.100	2.00	1.65	8.52
0.100	2.00	1.03	8.50
0.100	0.686	0.206	8.57
0.100	0.790	0.237	10.2[b]
0.300	2.00	1.85	23.5
0.300	2.00	0.820	23.8
0.300	2.00	0.830	27.0[c]
0.300	2.00	1.24	23.0
0.300	1.72	0.515	23.1

[a] Acetone–water (1:1, v/v), at 25.0° with $\mu = 1.00\ M$. [b] $[Fe(C_2H_5)_2^+]_0 = 1.0 \times 10^{-3}\ M$. [c] $[Fe(C_5H_5)_2^+]_0 = 2.0 \times 10^{-4}\ M$.

$$\frac{-d[Cr(VI)]}{dt} = \frac{-d[Fe(C_5H_5)_2]}{3dt} = k'[Fe(C_5H_5)_2][Cr(VI)] \qquad (3)$$

The values of k' increase significantly with $[H^+]$, however.

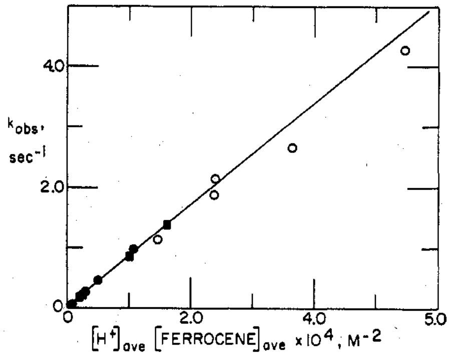

Figure 1.—A plot of the pseudo-first-order rate constant assuming a direct proportionality to $[H^+]$ and $[Fe(C_5H_5)_2]$. Plotted in this form, allowance for K_a has not been made. The symbols refer to different $[H^+]$: 0.050 M (filled circles), 0.10 M (squares), and 0.30 M (open circles).

To a good approximation the value of k' appears to be directly proportional to $[H^+]$; Figure 1 depicts a plot of k_{obsd} *vs.* the product $[H^+][Fe(C_5H_5)_2]_{av}$. This suggests the rate expression

$$-d[Cr(VI)]/dt = k[Fe(C_5H_5)_2][HCrO_4^-][H^+] \qquad (4)$$

where $HCrO_4^-$ (the predominant species) is related to the total Cr(VI) concentration by the expression

$$[HCrO_4^-] = [Cr(VI)]_T\{K_a/K_a + [H^+]\} \qquad (5)$$

which makes allowance for the formation of small quantities of H_2CrO_4.[6]

Combination eq 3–5 leads to the result

$$k' = \frac{k[H^+]K_a}{K_a + [H^+]} \qquad (6)$$

Treatment of the data in Table II as suggested by eq 6 gives the result $k = 1.01 \pm 0.04 \times 10^4\ M^{-2}$ sec^{-1} and $K_a = 1.06 \pm 0.25\ M$. Although this result cannot be regarded as an accurate determination of K_a in this medium, it does show that the value needed to account for the H^+ dependence of the apparent rate constant is a reasonable one considering the value in water.[6]

Consequently it is concluded that the major rate determining step is represented by the rate expression given by eq 4, according to which the composition of the transition state is $[Fe(C_5H_5)_2H_2CrO_4]^{\ddagger}$, suggesting the rate determining step

$$Fe(C_5H_5)_2 + HCrO_4^- + H^+ \longrightarrow Fe(C_5H_5)_2^+ + H_2CrO_4^{2-} \qquad (7)$$

The most logical steps following eq 7 needed to complete the stoichiometry are

$$Fe(C_5H_5)_2 + Cr(V) \longrightarrow Fe(C_5H_5)_2^+ + Cr(IV) \qquad (8)$$

$$Fe(C_5H_5)_2 + Cr(V) \longrightarrow Fe(C_5H_5)_2^+ + Cr(III) \qquad (9)$$

Mechanisms in place of eq 7–9 involving a two-

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(6) The equilibrium $H_2CrO_4 \rightleftharpoons H^+ + HCrO_4^-$ has K_a ~4.2 M in water at 25° [J. Y. Tong, *Inorg. Chem.*, **3**, 1804 (1964)], which suggests that only a relatively small fraction of Cr(IV) exists as H_2CrO_4 in the range 0.05–0.30 M H^+. Species such as $Cr_2O_7^{2-}$ are of negligible importance at the low Cr(VI) concentrations employed.

equivalent step are disfavored since further oxidation of $Fe(C_5H_5)_2^+$ results in irreversible decomposition, whereas it has been shown here that the expected yield of ferricenium ion is obtained quantitatively. Furthermore, the chronopotentiometric oxidation of ferrocene is a one-equivalent reversible conversion to ferricenium ion; even potentials as high as +1.4 V *vs.* sce did not produce a second oxidation wave.[7]

The effect of the product, $Fe(C_5H_5)_2^+$, was studied in two experiments as shown in Table II. Its concentration was increased considerably compared to the other runs and no retarding effect was found, supporting eq 7 and not eq 8 or 9 as the rate determining step. This is in agreement with the mechanism in other instances where the reducing agent is not a complex which undergoes rapid ligand substitution.[5,8]

If $Fe(C_5H_5)_2^+$ exerts any effect at these high concentrations it is to increase the rate of reaction by a small amount. This phenomenon might be rationalized by a product-catalysis term,[9] but the effect was not explored in detail. In any event the possible existence of this term is not sufficient to cause us to question the conclusion from the present work that the oxidation of ferrocene by chromium(VI) occurs in a sequence of one-equivalent steps with the first such step the slowest.

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Cyanophosphine Complexes of Nitrosylcobalt Carbonyl

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It is well understood that the C–O antibond orbitals in a metal carbonyl can accept metal d electrons, causing lower C–O stretching frequencies than would occur without such metal→carbon back-bonding. However, since the CO ligands are competing for the back-bonding d electrons, some replacement of CO by a weaker acceptor ligand leads to better acceptor action by the remaining CO ligands, further decreasing their stretching frequencies.[1] For example, aminophosphines or alkylphosphines are dramatically effective as replacement ligands which lower the C–O frequencies. Stronger π-acceptor ligands such as PF_3 or trifluoromethylphosphines are less effective for lowering the C–O frequencies,[2] but the rule has been that some significant decrease always results from replacement of CO by any phosphine.

We now have tried three cyanophosphines as ligands for single replacement of CO in $NOCo(CO)_3$, finding that the resulting $LCoNO(CO)_2$ complexes have some of the highest C–O stretching frequencies yet observed for such compounds—in one mode even higher than in pure $NOCo(CO)_3$. It appears that these ligands are more effective than any previously used, for attracting metal 3d electrons and so minimizing the interaction of such electrons with the CO antibonding orbitals. The significant infrared frequencies (cm^{-1}, vapor phase) are compared in Table I.

TABLE I

COMPARISON OF PERTINENT INFRARED FREQUENCIES (CM^{-1}) OF $LCoNO(CO)_2$ COMPOUNDS

	L					
	CO	PF_3[a]	$(CF_3)_3P$	$(CF_3)_2P$-CN	CF_3P-$(CN)_2$	$P(CN)_3$
C–N str				2192 (2194)[b]	2198 (2197)[b]	2200 (2179)[b]
C–O in-phase str	2108	2087	2088	2095	2098	2102
C–O out-of-phase str	2047	2044	2043	2055	2058	2064
N–O str	1822	1825	1832	1833	1833	1833

[a] I. H. Sabherwal and A. B. Burg, *Chem. Commun.*, 854 (1969).
[b] The parenthetical numbers refer to the free ligands.

The nearly unchanged C–N stretching frequencies show that the ligand action is through P rather than CN in all cases. It also seems that the positive and negative effects of ligand action, upon the C–N frequencies, are fairly well balanced.

One such effect would be delocalization of the metal 3d electrons across phosphorus into the σ- and π-antibonding orbitals of the CN group. This would account for the extreme electron-withdrawing effect, indicated by the high C–O stretching frequencies, while the effect upon the C–N stretching frequency would be negative. A compensating positive effect concerns the phosphorus lone-pair electrons. In the free cyanophosphine, these are expected to interact with the C–N antibond orbitals; hence their reemployment for σ bonding to the metal would lead to higher C–N stretching frequencies. Ostensibly, these two effects nearly balance each other except in the case of $P(CN)_3$. However, the cogency of this argument is diminished by a third variable: one cannot be sure about how much the C–N stretching frequency is affected by tetrahedral rehybridization of phosphorus. In sum, there is no good argument against the idea of delocalization of metal electrons into the C–N antibonding orbitals, a hypothesis which is needed to explain the present results.

Ligand Synthesis and Characterization.—The iodophosphines $(CF_3)_2PI$ and CF_3PI_2 were converted by $Hg(CN)_2$ (moderate excess, sealed tubes, 8 hr, 40–60°) to $(CF_3)_2PCN$ and $CF_3P(CN)_2$ in 99–100% yields. The end of each process was indicated by decolorization of the liquid. Our attempts to use AgCN for the same conversion[3] gave unaccountably erratic results. For the conversion of PCl_3 to $P(CN)_3$, however, the AgCN method[4] was chosen to avoid contamination by $HgCl_2$. We employed excess PCl_3 in a sealed tube (28 hr, 180°), obtaining a 57% yield of $P(CN)_3$, which was isolated by high-vacuum sublimation at bath temperatures up to 90°.

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