present indicating a more complicated reaction than found for $KCrO_3Cl$.

Preparation of $KCrO_2(ClCF_2COO)_3$.—To 2.50 mmol of $K_2Cr_2O_7$, 25 mmol of $(ClCF_2CO)_2O$ was added. The red-brown product [4.94 mmol of $KCrO_2(ClCF_2COO)_3$] was formed at room temperature (0.25 hr) in 99% yield; mp 124–126°.

The powder spectrum gave the following *d* values (in Å) with their respective intensities: 11.27 (s), 9.20 (s), 6.01 (vs), 5.29 (m), 5.03 (s), 3.97 (vs), 3.74 (m), 3.63 (m), 3.54 (m), 3.05 (m). *Anal.* Calcd for $KCrO_2(ClCF_2COO)_3$: Cr, 10.1. Found: Cr, 9.5 *via* iodometry, 10.1 *via* acidity (based on eq 3).

Preparation of $K_2CrO_2(CF_3COO)_4$.—To 2.945 mmol of K_2CrO_4, 50 mmol of TFAA was added. The red solid [2.980 mmol of $K_2CrO_2(CF_3COO)_4$] was formed at room temperature (24 hr) in 100% yield. It was possible at room temperature to isolate a tan product $K_2CrO_2(CF_3COO)_4\cdot 0.7(CF_3CO)_2O$, but heating to 60° gave $K_2CrO_2(CF_3COO)_4$; mp 95–105°.

The powder spectrum gave the following *d* values (in Å) with their respective intensities: 11.87 (s), 9.910 (m), 8.908 (m), 5.023 (m), 4.599 (m), 4.471 (m), 4.081 (vs), 3.966 (m), 3.850 (m). *Anal.* Calcd for $K_2CrO_2(CF_3COO)_4$: C, 15.6; F, 37.1; Cr, 8.5. Found: C, 15.4; F, 36.5; Cr, 8.8, 8.48 *via* iodometry, 8.51 *via* acidity (based on eq 3).

Preparation of $K_2CrO_2(C_3F_7COO)_4$.—To 4.14 mmol of K_2CrO_4, 12.33 mmol of $(C_3F_7CO)_2O$ was added. The red-brown product [4.37 mmol of $K_2CrO_2(C_3F_7COO)_4$] was formed at room temperature (24 hr) but prolonged heating at 60–100° was necessary for complete removal of anhydride; mp ~73–78°. At room temperature the product corresponded to $K_2CrO_2(C_3F_7COO)_4\cdot(C_3F_7CO)_2O$.

The powder spectrum gave the following *d* values (in Å) with their respective intensities: 9.86 (m), 6.80 (s), 2.95 (m), 2.57 (s), 2.41 (m), 2.296 (m). *Anal.* Calcd for $K_2CrO_2(C_3F_7COO)_4$: C, 18.9; F, 52.4; Cr, 5.14. Found: C, 19.0; F, 52.4; Cr, 4.97.

Preparation of $Cs_2CrO_2(CF_3COO)_4$.—To 2.4 mmol of C_2CrO_4, 45 mmol of $(CF_3CO)_2O$ was added. The dark yellow product [2.23 mmol of $Cs_2CrO_2(CF_3COO)_4$] was formed at room temperature (3 hr) in 99% yield and heating at ~40° removed any excess TFAA; mp 71–73°.

The powder spectrum gave the following *d* values (in Å) with their respective intensities: 4.67 (m), 4.04 (s), 3.92 (s), 3.74 (s), 3.52 (s), 3.38 (s), 2.51 (vs). *Anal.* Calcd for $Cs_2CrO_2(CF_3COO)_4$: C, 12.0; F, 28.4; Cr, 6.5. Found: C, 11.6; F, 28.1; Cr, 7.0, 6.50 *via* iodometry, 6.52 *via* acidity (based on eq 3).

Preparation of $NH_4CrO_2(CF_3COO)_3$.—To 5.65 mmol of $(NH_4)_2Cr_2O_7$ in ~20 ml of Freon 113, ~23 mmol of TFAA was added. The red product [11.55 mmol of $NH_4CrO_2(CF_3COO)_3$] was formed at room temperature (~20 hr) in 100% yield. The product decomposed above 70°.

The powder spectrum gave the following *d* values (in Å) with their respective intensities: 12.30 (m), 9.688 (s), 7.468 (m), 6.661 (s), 6.146 (s), 5.480 (m), 5.035 (vs), 4.638 (s), 4.507 (m), 4.116 (vs), 3.966 (vs), 3.705 (s). *Anal.* Calcd for $NH_4CrO_2(CF_3COO)_3$: C, 16.4; H, 0.9; N, 3.18; F, 38.9; Cr, 11.8. Found: C, 16.2; H, 1.2; N, 3.34; F, 39.0; Cr, 12.0.

Preparation of $Ag_2CrO_2(CF_3COO)_4$.—To 1.05 mmol of Ag_2CrO_4, 22 mmol of TFAA was added. The brown product [1.01 mmol of $Ag_2CrO_2(CF_3COO)_4$] was formed at room temperature (1 hr) in 99% yield. The product decomposed above 200°.

The powder spectrum gave the following *d* values (in Å) with their respective intensities: 14.88 (s), 6.33 (m), 6.12 (s), 3.64 (s), 3.48 (m), 3.00 (m), 2.88 (vs), 2.84 (m), 2.59 (m), 2.34 (s), 2.29 (m).

Preparation of $PbCrO_2(CF_3COO)_4$.—To 2.74 mmol of $PbCrO_4$, 17.6 mmol of $(CF_3CO)_2O$ was added. The red-brown solid [2.88 mmol of $PbCrO_2(CF_3COO)_4$] was formed at ~50° (15 hr). Heating at 50° was needed for complete removal of excess $(CF_3CO)_2O$; mp 80–87°.

The powder spectrum showed the material to be amorphous. *Anal.* Calcd for $PbCrO_2(CF_3COO)_4$: C, 12.9; F, 30.7; Cr, 7.00; Pb, 27.9. Found: C, 12.7; F, 30.7; Cr, 7.01; Pb, 27.9.

Preparation of $Na_2MoO_2(CF_3COO)_4$.—To 2.87 mmol of Na_2MoO_4, 34 mmol of TFAA was added. The white amorphous solid product [2.90 mmol of $Na_2MoO_2(CF_3COO)_4$] was formed at 40–50° (20 days) in 99% yield; mp 80° dec. This solid has an amorphous structure (no lines in X-ray powder spectrum). *Anal.* Calcd for $Na_2MoO_2(CF_3COO)_4$: C, 15.3; F, 36.4; Mo, 15.3. Found: C, 15.2; F, 35.9; Mo, 15.3.

Preparation of $Na_2WO_2(CF_3COO)_4$.—To 1.71 mmol of Na_2WO_4, 35 mmol of TFAA was added. The white solid product [1.64 mmol of $Na_2WO_2(CF_3COO)_4$] was formed at 40–50° (7 days) in 96% yield; mp 98–102°.

The powder spectrum gave the following *d* values (in Å) with their respective intensities: 12.44 (vs), 10.91 (m), 4.24 (m), 3.54 (m), 2.37 (m). *Anal.* Calcd for $Na_2WO_2(CF_3COO)_4$: C, 13.4; F, 31.9; W, 25.8. Found: C, 11.1; F, 27.6; W, 25.6 *via* acidity (based on eq 3).

$K_2CrO_2(CF_3COO)_4$–HSO_3F Reaction.—To 6.57 mmol of $K_2CrO_2(CF_3COO)_4$ in a ~200-ml Pyrex-glass vessel equipped with a Kontes Teflon stopcock, 97.5 mmol of freshly distilled HSO_3F was added. Upon warming to room temperature a clear, dark reddish brown solution was produced. After approximately 1 day at room temperature, the volatile materials were pumped away through a trap cooled to $-195.8°$ (28.1 mmol lost *vs.* 26.1 mmol (theory) for CF_3COOH). An infrared spectrum showed the volatile material to be essentially CF_3COOH. The reaction vessel was warmed to 50–60° and pumped on in order to remove the slightly volatile HSO_3F. Pumping to constant weight left a brown solid [6.62 mol of product].

The powder spectrum gave the following *d* values (in Å) with their respective intensities: 4.57 (m), 3.67 (s), 3.45 (vs), 3.37 (m), 3.13 (vs), 2.91 (vs), 2.78 (m), 2.58 (m), 2.51 (s), 2.28 (m), 2.20 (s), 2.17 (m), 2.09 (m) 2.05 (s), 1.76 (m), 1.68 (s), 1.36 (s). The infrared spectrum gave the following absorption bands (in cm^{-1}): 1275 (vs), 1088 (w), 943 (w). *Anal.* Calcd for $K_2CrO_2(SO_3F)_4$: S, 22.9; F, 13.6; Cr, 9.3. Found: S, 22.7; F, 13.5; Cr, 9.3.

CrO_3–$(CF_3CO)_2O$–CF_3COOK Reaction.—To 19.77 mmol of CrO_3, 42.4 mmol of CF_3COOK and an excess of 105 mmol of $(CF_3CO)_2O$ were added. The dark red solid [19.54 mmol of $K_2CrO_2(CF_3COO)_4$] was formed at room temperature (41 hr).

The X-ray powder photograph was essentially the same as found for $K_2CrO_2(CF_3COO)_4$.

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Disproportionation of Ammine(pyridine)ruthenium(II) Complexes in Alkaline Solution

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Ammine(pyridine)ruthenium(II) complexes are deeply colored owing to a strong charge-transfer absorption band in the visible region of the spectrum, while the corresponding complexes of Ru(III) are almost colorless.[2] We have observed that when the pH of a solution containing a Ru^{III}–py complex is raised to about 8 or above, a strong color develops. The absorption spectrum of the colored solution in the visible region of the spectrum closely resembles that of Ru(II), at least if the spectrum is taken soon after the solution of Ru(III)

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[1] NSF Science Faculty Fellow, Stanford University, 1967.

[2] P. Ford, D. P. Rudd, R. Gaunder, and H. Taube, *J. Amer. Chem. Soc.*, **90**, 1187 (1968).

is made alkaline. The phenomenon has been observed with various complexes of the type $Ru^{III}(NH_3)_5L$ where L may be pyridine, pyrazine, 4-pyridinecarbinol, 4-pyridinecarboxaldehyde, or isonicotinate. On the basis of the evidence to be outlined, we have concluded that the reaction producing the change in color is the disproportionation 2Ru(III) = Ru(II) + Ru(IV). Ruthenium(IV) is expected to be much more acidic than is Ru(III) or Ru(II), and the effect of pH on the equilibrium can be ascribed to proton removal from NH_3 coordinated to Ru(IV).

Experimental Section

The experiments were done on the complex $Ru(NH_3)_5py^{3+}$ (hereafter represented as $Ru^{III}py$) used at concentrations between 10^{-4} and 10^{-3} *M*. The concentration of $Ru^{III}py$ was estimated making use of the absorption bands at 248, 256, and 261 nm. The product Ru^{II}–py species (to be represented as $Ru^{II}py$, a designation which will include all Ru^{II}–pyridine complexes) was analyzed using light at 407 nm, the maximum in the charge-transfer band for $Ru(NH_3)_5py^{2+}$. It should be noted that the intensity of absorption at this wavelength is only weakly sensitive to replacement of NH_3 by H_2O[3] but is very sensitive to release of pyridine from Ru(II) and to oxidation of Ru(II).

The formation of $Ru^{II}py$ from $Ru^{III}py$ was found to be partially reversible under all conditions. In two experiments using $NaHCO_3$ as base (pH 8.0) about 10 and 15%, respectively, of the $Ru^{III}py$ transformed to $Ru^{II}py$ after 60–120 min, and these appeared to be limiting amounts. Deoxygenated N_2 was then passed through to remove O_2 and a solution of deoxygenated $HClO_4$ was added. In one experiment 95% and in the other 75% of the $Ru^{II}py$ which had been produced disappeared on acidification, the reaction appearing to be complete in 5 min.

However, in an experiment in 0.067 *M* NaOH, after 42% of the original $Ru^{III}py$ had transformed to $Ru^{II}py$, on adding $HClO_4$ only 12% of the total ruthenium was accounted for by the $Ru^{II}py$ which disappeared, the remaining $Ru^{II}py$ accounting for 30% of the total ruthenium.

In other experiments disproportionation was allowed to occur to various extents, then $HClO_4$ and Cr^{2+} were added to reduce all Ru to the 2+ oxidation state, and the Ru^{II} concentration was monitored. The results are indicated in Table I. A complication in these experiments was the fact that the 407-nm band used to monitor Ru^{II} was shifted toward the blue, in the worst case to 399 nm. This effect was undoubtedly caused by loss of NH_3 from the complexes.

Table I

Recovery of $Ru^{II}py$ after Disproportionation[a]

Buffer used	pH	% $Ru^{III}py$ converted to $Ru^{II}py$ by disproportionation	Amt of $Ru^{II}py$ after Cr(II) reduction, % of total Ru	Time $Ru^{III}py$ allowed to react, min
Arsenate	9.06	30	93	120
Carbonate	9.60	48.6	98	100
Carbonate	9.54	47.5	93	100

[a] The initial concentration of $Ru^{III}py$ was (1–2) × 10^{-4} *M*.

In all cases the course of the reaction was as follows. The concentration of $Ru^{II}py$ increased, reached a maximum, and then decreased. The rate and the proportion of $Ru^{III}py$ converted to $Ru^{II}py$ both increased with pH, but the proportion converted never exceeded 50%. Results on extent of conversion are listed in Table II.

The rate of disproportionation was followed in two buffer mixtures: HCO_3^-–CO_3^{2-}, pH 9.6; $H_2AsO_4^-$–$HAsO_4^{2-}$, pH 8.3. In each series the pH and buffer concentrations were held constant, but the initial concentration of Ru(III) was varied. The specific rates recorded for the two sets corresponding to the rate law $-d[Ru(III)]/dt = k[Ru(III)]^2$ at 25° were as follows: carbonate buffer, $10^4[Ru(III)]_0 = 1.12, 1.64, 2.50, 3.13, 4.65$ *M*; $k = 2.9, 2.6, 2.4, 2.9, 2.5$ M^{-1} sec^{-1}, respectively; arsenate buffer, $10^4[Ru(III)]_0 = 1.08, 1.79, 2.48, 3.96$ *M*; $k = 0.37, 0.32, 0.30, 0.32$ M^{-1} sec^{-1}, respectively. These measurements serve to show that the specific rate is independent of $[Ru(III)]_0$; they do not define the actual values of the rate constants because the buffer concentration was not accurately fixed. (It was on the order of 0.1 *M* in total carbonate or total arsenate.)

Table II

Extent of Disproportionation of $Ru^{III}py$

Buffer used	pH	% of original $Ru^{III}py$ present as $Ru^{II}py$ at the point of max concn
$NaHCO_3$	8.0	17
$NaHCO_3$	8.6	31
NH_3, NH_4ClO_4[a]	9.0	41.5
HCO_3^-, CO_3^{2-}	9.5	47.5
HCO_3^-, CO_3^{2-}	9.6	48.6
0.067 *M* NaOH		42.0

[a] Saturated in NH_4ClO_4.

In both carbonate and arsenate buffers new ruthenium complexes formed as indicated by bands at 524 nm (arsenate) and 558 nm (carbonate). These bands were not formed from $Ru^{III}py$ in acid solution nor from $Ru^{II}py$ in basic buffers. They could not be correlated with any known complexes of ruthenium.

Discussion

The following conclusions can be drawn from the observations with some assurance.

1. $Ru^{III}py$–ammine complexes disproportionate in basic solution giving the corresponding $Ru^{II}py$ complexes. This process is reversible if the time of the reaction is not too long and the basicity is not too great.

2. The other product is a $Ru^{IV}py$ complex. This conclusion is indicated by the fact that the $Ru^{II}py$ concentration approaches, but never exceeds, 50% of the initial $Ru^{III}py$ concentration. It is also indicated by the fact that the formation of $Ru^{II}py$ is second-order in $Ru^{III}py$.

3. The initial Ru(IV) complex is derived from $Ru^{III}py$ by loss of protons from coordinated NH_3. The intervention of a process such as this is needed to explain the pH dependence of the equilibrium.

4. The Ru(IV) complex is labilized by base as shown by attempts to restore $Ru(NH_3)_5py^{3+}$. This could be done at pH 8–8.5 but not above pH 9.0. In very basic solution even the oxidizing power of Ru^{IV} seemed to disappear almost completely.

5. The bands at 524 nm (arsenate) and 558 nm (carbonate) are probably due to Ru(IV) complexes. The bands are not formed from Ru(II) and the anion. No bands in this region are expected for Ru(III) complexes. Complexes of Ru(IV) are known to have visible ligand to metal charge-transfer bands.

Apart from the specific conclusions reached, the experiments show that ruthenium(III) ammines are not tractable at moderate to high pH's, at least when pyridine is in the coordination sphere. This conclusion may well extend also to hexaammine- and aquopentaammineruthenium(III).

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