dissociate. However, removal of excess CH_3CN under vacuum from a solution of NiL_3 in acetonitrile gave a brownish white solid foam, which dissolved in benzene to give an orange solution, in ether to give a yellow solution, and in hexane to give a light yellow solution.[8] In methanol the starting NiL_3 complex precipitated as a red powder. The proton nmr spectrum of the orange solution (C_6D_6) showed four resonances at τ 2.28, 3.16, 7.93, and 9.44 in a ratio of 9:27:27:3 as expected for the ortho H of L, unresolved meta and para H's of L, CH_3 of L, and CH_3CN, respectively, in the complex $(CH_3CN)Ni[P(O\text{-}o\text{-}C_6H_4CH_3)_3]_3$. Addition of CH_3CN to the solution caused the highest field resonance to shift toward the free CH_3CN position at τ 9.29, without appreciably affecting the resonances due to L, in agreement with the very rapid exchange of free and complexed CH_3CN in eq 1 proposed on the basis of the ^{31}P experiments.

That nitrile complexes of Ni(0) form with other phosphorus ligands was shown by the rapid color change of a red toluene solution of $Ni(P(C_6H_5)_3)_3$ to yellow on addition of excess CH_3CN. We have been unable to see the ν_{CN} band of $(CH_3CN)Ni(P(C_6H_5)_3)_3$ in the infrared spectrum, possibly because it is masked by the free CH_3CN.

The formation of nitrile complexes of Ni(0) with the phosphorus ligands $P(O\text{-}o\text{-}C_6H_4CH_3)_3$ or $P(C_6H_5)_3$ is facilitated since their three-coordinate nickel complexes have a free coordination position, ready to accept a nitrile to give the metal an 18-electron inert gas configuration. Four-coordinate nickel complexes, such as $Ni[P(OC_2H_5)_3]_4$, which do not dissociate detectably in solution,[4] show no evidence of complex formation with nitriles even when present in large excess.

Experimental Section

All preparations were done under an N_2 atmosphere in a vacuum Atmosphere drybox. The nickel complexes and their solutions are very sensitive to O_2 of air. The ^{31}P nmr spectra were recorded at 40.5 Mc using a Varian HA-100 spectrometer. Chemical shifts were measured using a concentric capillary of P_4O_6 and are reported with respect to 85% H_3PO_4, after subtracting 112.5 ppm from the measured values. Proton nmr spectra were recorded at 60 Mc on a Varian A-60 spectrometer using tetramethylsilane as an internal reference in C_6D_6. Infrared spectra were recorded with 0.1-mm NaCl cells using a Perkin-Elmer 221 spectrometer; spectra were calibrated with CO gas. Optical spectra were recorded with a Cary 14 spectrometer using quartz cells of 0.1- and 1-mm path length and a 1-mm thermostated cell (Optical Cell Co., Inc.). Water circulated from a Forma constant-temperature bath was used to maintain the temperature in the thermostated cell to ±0.5°.

The complexes $Ni[P(O\text{-}o\text{-}C_6H_4CH_3)_3]_3$[3] and $Ni(P(C_6H_5)_3)_3$[9] were prepared by literature methods. The solvents and nitriles were reagent grade. The crude product $(CH_3CN)Ni[P(O\text{-}o\text{-}C_6H_4CH_3)_3]_3$ prepared by removal of excess CH_3CN under vacuum from $Ni[P(O\text{-}o\text{-}C_6H_4CH_3)_3]_3$ melted to a red liquid at 50–80° and blackened over 100° (sealed evacuated capillary). *Anal.* Calcd for $C_{65}H_{66}NNiO_9P_3$: C, 67.5; H, 5.8; N, 1.2; Ni, 5.1. Found: C, 66.0; H, 5.8; N, 1.2; Ni, 4.6.

Acknowledgments.—The author is indebted to Dr. W. C. Seidel for preparation of pure samples of the NiL_3 complexes and to Mrs. Jean L. Read for running the nmr spectra.

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[8] The dependence of the color of the solution on the solvent indicates that $(CH_3CN)NiL_3$ dissociates more extensively in more polar solvents. From the electronic spectra, we expect the pure $(CH_3CN)NiL_3$ complex to be colorless.

[9] B. Bogdanovic, M. Kröner, and G. Wilke, *Justus Liebigs Ann. Chem.*, **699**, 1 (1966).

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The Reaction of Metal Oxide Salts with Fluorinated Anhydrides[1]

BY J. N. GERLACH AND G. L. GARD*

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Recently, it was found[2] that chromium trioxide reacts with fluorinated anhydrides according to the equation

$$CrO_3 + (R_fCO)_2O = CrO_2(R_fCOO)_2 \quad (1)$$

where $R_f = CF_3$, $ClCF_2$, or C_3F_7.

In our investigations with other chromium(VI) oxy compounds an attempt was made to replace the chloro group in $KCrO_3Cl$. Surprisingly it was found that, as well as replacing the chloro group, addition across the chromium–oxygen multiple bond occurred according to the equation

$$KCrO_3Cl + 2(CF_3CO)_2O \longrightarrow KCrO_2(CF_3COO)_3 + CF_3COCl \quad (2)$$

We have studied other salt systems as well as other fluorinated anhydrides in order to determine the scope of this reaction. The results of this work are presented in Table I. It is seen that not only Cr(VI) salts but other group VIb oxy(transition metal) salts (with high positive oxidation states) are also reactive.

The new chromium salts in Table I are usually red-brown solids which are soluble in excess $(CF_3CO)_2O$ and are not extremely stable [*e.g.*, $K_2CrO_2(CF_3COO)_4$ decomposes above 150°] toward heat or light.

TABLE I

Salt	Anhydride	Product(s)
$KCrO_3Cl$	$2(CF_3CO)_2O$	$KCrO_2(CF_3COO)_3 +$ CF_3COCl
$K_2Cr_2O_7$	$3(CF_3CO)_2O$	$2KCrO_2(CF_3COO)_3$
$K_2Cr_2O_7$	$3(ClCF_2CO)_2O$	$2KCrO_2(ClCF_2COO)_3$
K_2CrO_4	$2(CF_3CO)_2O$	$K_2CrO_2(CF_3COO)_4$
K_2CrO_4	$2(C_3F_7CO)_2O$	$K_2CrO_2(C_3F_7COO)_4$
Cs_2CrO_4	$2(CF_3CO)_2O$	$Cs_2CrO_2(CF_3COO)_4$
$(NH_4)_3Cr_2O_7$	$3(CF_3CO)_2O$	$2NH_4CrO_2(CF_3COO)_3$
Ag_2CrO_4	$2(CF_3CO)_2O$	$Ag_2CrO_2(CF_3COO)_4$
$PbCrO_4$	$2(CF_3CO)_2O$	$PbCrO_2(CF_3COO)_4$
Na_2MoO_4	$2(CF_3CO)_2O$	$Na_2MoO_2(CF_3COO)_4$
Na_2WO_4	$2(CF_3CO)_2O$	$Na_2WO_2(CF_3COO)_4$

All of the compounds are very water sensitive with the chromium compounds hydrolyzing according to the generalized equation

$$M_{1\,\mathrm{or}\,2}CrO_2(R_fCOO)_{3\,\mathrm{or}\,4} + 2H_2O = (1\text{ or }2)M^+ + CrO_4^{2-} + (3\text{ or }4)R_fCOO^- + 4H^+ \quad (3)$$

($M^+ = K^+, Cs^+, NH_4^+$; $R_f = CF_3, ClCF_2, C_3F_7$). The infrared spectra were measured neat between NaCl windows and are listed in Table II. On the basis of the results of Sharp and coworkers[3] for anhydrous transition metal trifluoroacetates, the various absorption bands were assigned for the oxy(transition metal) trifluoroacetates. The COO asymmetric stretch occurs at 1670–1700 cm^{-1}, COO symmetric stretch at 1320–

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[1] Presented at the 25th Regional Meeting of the American Chemical Society, Seattle, Wash., 1970.

[2] J. N. Gerlach and G. L. Gard, *Inorg. Chem.*, **9**, 1565 (1970).

[3] M. J. Bailie, D. H. Brown, K. C. Moss, and D. W. A. Sharp, *J. Chem. Soc. A*, 3110 (1968).

TABLE II
INFRARED SPECTRA OF SOLIDS (CM^{-1})

$KCrO_2$-$(CF_3COO)_3$	K_2CrO_2-$(CF_3COO)_4$	$KCrO_2$-$(ClCF_2COO)_3$	K_2CrO_2-$(C_3F_7COO)_4$
1670 s	1680 s	1680 s, b	1653 s, b
1380 s	1380 m	1320 m	1300 m
1160 s, b	1150 s, b	1140 s, b	1200 s, b
950 m	940 m	950 s, b	1138 s
875 w	880 w	840 w	1110 m
845 w	780 w	815 w	1070 m
780 m	725 w	720 m	950 m
725 m–s	705 m		923 m
			813 w
			699 m

$NH_4CrO_2(CF_3COO)_3$	$Cs_2CrO_2(CF_3COO)_4$	$Ag_2CrO_2(CF_3COO)_4$
3100 s	1670 s, b	1690 s
1700 s	1370 m	1440 m
1400 s	1150 s, b	1200 s, b
1170 vs	940 m	970 m
940 s	780 w	850 w
860 w	725 w	795 m
785 m	705 w	730 m–s
725 m		

$PbCrO_2(CF_3COO)_4$	$NaWO_2(CF_3COO)_4$	$Na_2MoO_2(CF_3COO)_4$
1626 s, b	1650 s	1660 s, b
1426 m	1450 m	1390 m
1163 vs, b	1320 w	1150 s, b
925 w	1160 s, b	960 w
855 m	805 w	915 m
795 m	725 w	845 w
724 m	705 w	780 m
693 w		720 m

1440 cm^{-1}, C–F asymmetric stretch at 1140–1200 cm^{-1}, C–C stretch at 840–875 cm^{-1}, CF_3 symmetric stretch at 780–795 cm^{-1}, and CCO_2 in-plane bend at 705–730 cm^{-1}.

For all the oxychromium salts the absorption band at 940–970 cm^{-1} probably represents the stretching frequency for the Cr–O–C vibration. For CrO_3 this vibration (actually Cr–O–Cr) is at 893 cm^{-1}. For all compounds studied the absorption bands attributed to M=O vibration are absent.[4]

The powder spectra were taken in order to ensure that all of the reactant salt was consumed and that each product was in fact different. The X-ray results are presented in the Experimental Section and do confirm the uniqueness of each compound.

With a very strong acid, HSO_3F, all of the trifluoroacetate groups of $K_2CrO_2(CF_3COO)_4$ are replaced according to the equation

$$K_2CrO_2(CF_3COO)_4 + 4HSO_3F = K_2CrO_2(SO_3F)_4 + 4CF_3COOH \quad (4)$$

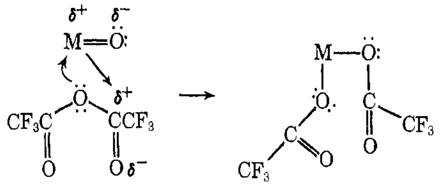
The driving force for this reaction is apparently the formation of the weaker acid CF_3COOH in this system.

Alternate and useful methods for preparing these compounds involve the application of the Usanovich theory.[5] In trifluoroacetic anhydride, chromyl trifluoroacetate should behave as an acid toward the basic potassium trifluoroacetate according to the equation

$$CrO_2(CF_3COO)_2 + 2CF_3COOR \xrightarrow{(CF_3CO)_2O} K_2CrO_2(CF_3COO)_4 \quad (5)$$

This was found to be correct and affords another route to dioxopolyfluoroacetatochromium(VI) salts.

It is rather unusual that fluoroanhydrides will effectively add across the M=O multiple bond while hydrocarbon anhydrides will not. A mechanism which would envisage a possible pathway is



The CF_3 group induces a partial positive charge on the carbonyl carbon which facilitates interaction with the π electrons in the M=O linkage. In hydrocarbon anhydrides this inductive effect is absent.

In addition to group VIb oxy(transition metal) salts the fluoroanhydrides appear to react with group Vb and group VIIb oxy salts. Further studies are in progress.

Experimental Section

Chemicals and Equipment.—The salts used in this study were either reagent grade or at least 98% pure. They were thoroughly dried before use. $(CF_3CO)_2O$ was dried over P_2O_5 and distilled before use. The other anhydrides were used as received and infrared spectra confirmed their purity. The infrared spectra were recorded on a Perkin-Elmer 137 infrared spectrophotometer.

X-Ray powder spectra were obtained using an XRD-5 General Electric camera. Nickel-filtered copper radiation (Cu Kα radiation) was used. The procedure was standardized using known compounds (CrO_3, Cr_2O_3, $CrF_3 \cdot 3H_2O$) in which the calculated *d* values agreed with the published ASTM values. Only the very strong (vs), strong (s), and medium (m) intensity lines are reported in this paper.

Chemical Analyses.—The chromium content was determined iodometrically, after hydrolysis, by quantitatively reducing chromic acid to trivalent chromium. The acidity was determined by titration with a standard base solution using phenolphthalein indicator. Standard analyses were performed by Beller Laboratory, Göttingen, West Germany.

General Procedure.—The reaction vessels (Pyrex glass) used in the following synthetic runs had volumes of 100 or 200 ml and were equipped with a Kontes Teflon stopcock and a Teflon-covered stirring bar.

The metal oxide salt was transferred to a vessel and then dried *in vacuo*, special care being taken for hygroscopic solids. Excess trifluoroacetic anhydride, $(CF_3CO)_2O$, TFAA, was then added. The mixture was warmed to room temperature and at room temperature was magnetically stirred. After the reaction was complete the volatile materials were removed by pumping through a trap cooled to −195.8° and the remaining solid was pumped until constant weight was achieved. For most reactions the constant weight was used to determine the composition of the solid product as no other products were formed.

Preparation of $KCrO_2(CF_3COO)_3$. Method 1.—To 6.21 mmol of $K_2Cr_2O_7$, 86.2 mmol of $(CF_3CO)_2O$ was added. The red-brown product [12.32 mmol of $KCrO_2(CF_3COO)_3$] was formed at room temperature (3 hr–3 days) in 99% yield, but heating at 50° was required for complete removal of TFAA. Upon heating, the solid became darker red and at 100–105° melting occurred.

The powder spectrum gave the following *d* values (in Å) with their respective intensities: 12.27 (s), 8.91 (m), 5.01 (s,) 4.58 (m), 4.45 (m), 4.04 (s), 3.95 (vs), 3.67 (m), 2.415 (m). *Anal.* Calcd for $KCrO_2(CF_3COO)_3$: C, 15.6; Cr, 11.3. Found: C, 14.0; Cr, 11.3, 10.7 *via* iodometry, 11.1 *via* acidity (based on eq 3).

Method 2.—To 4.5 mmol of $KCrO_3Cl$, 11 mmol of $(CF_3CO)_2O$ was added. After standing 1 day at room temperature the volatile materials were pumped away through a trap cooled to −195.8°. The brown product [4.66 mmol of $KCrO_2(CF_3COO)_3$] had a powder pattern vary similar to that for $KCrO_2(CF_3COO)_3$. An infrared spectrum of the volatiles showed CF_3COCl to be present.

Method 3.—To 4.86 mmol of $KCrO_3F$, 24 mmol of $(CF_3CO)_2O$ was added. After 5 hr at room temperature the volatile materials were pumped away through a trap cooled to −195.8° leaving behind a brown sticky solid [5.34 mmol of $KCrO_2(CF_3COO)_3$]. An infrared spectrum showed CF_3COF, CO_2, and COF_2 to be

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[4] C. G. Barraclough, J. Lewis, and R. S. Nyholm, *J. Chem. Soc.*, 3552 (1959).

[5] M. Usanovich, *J. Gen. Chem. USSR*, **9**, 182 (1939).

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).