ferences in solvent media and in ionic strength make comparisons questionable. However, on a qualitative basis it would seem that in a common system only Mg(II) has greater stability with acetylacetonate. Cd(II) and Zn(II) show greater stability for kojate, while the acetylacetonates and kojates of Co(II), Mn(II), Ni(II), and Cu(II) have relatively similar stabilities.

The lanthanide ions also show similar stabilities for these two ligands. This suggests that the increased stability of the five-membered ring formed by kojate complexing balances the expected stabilization of the acetylacetonate complexes due to the resonance in the chelate ring and to the greater basicity of this ligand. More detailed discussion of the relative complexing of these two ligands as well as of the more subtle question of the differences of the stability of the complexes as a function of atomic number of the lanthanide ions is not possible with free energy data alone.

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Some Reactions of Oxygen Difluoride

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As a part of a program of investigation of reactions of compounds containing the O–F group, a study has been made of reactions of oxygen difluoride, OF_2. The results are presented briefly here, but are given at length in a source available to all.[1]

One generalization which should be emphasized is that oxygen difluoride forms violently explosive mixtures with many substances.

Experimental

Basic Hydrolysis of Oxygen Difluoride.—Oxygen difluoride is known to react with dilute solutions of sodium hydroxide at about 0° and above to give oxygen and fluoride ion. If hypofluorite ion is formed, it decomposes rapidly giving oxygen. Since a low temperature should favor a low rate of decomposition, an attempt (which proved to be unsuccessful) was made to obtain hypofluorite ion by contacting oxygen difluoride with 40% KOH solution at −45° while stirring the liquid. Under these conditions the rate of production of oxygen was very low indeed, but the rate of absorption of oxygen difluoride, after saturation of the solution with OF_2, was also very low. If hypofluorite ion had been formed, oxygen fluoride should have dissolved rapidly and in large amount. The low rate of basic hydrolysis suggested the possibility that oxygen difluoride might be produced in high yield by the reaction of fluorine with 40% potassium hydroxide at −45°. This proved not to be the case. Yields about 9% of theoretical were obtained.

The reaction $OF_2 + 2\ OH^- \rightarrow H_2O + O_2 + 2F^-$ is known to be first order with respect to OF_2.[2] First-order rate constants were determined for the hydrolysis of oxygen difluoride in 40% potassium hydroxide while shaking the system, with the results shown in Table I.

TABLE I

HYDROLYSIS OF OF_2 IN 40% KOH

	248°K.	273°K.	293°K.
k (sec.$^{-1}$) for $-d(OF_2)/dt = k(OF_2)$	2.8×10^{-4}	9.5×10^{-4}	2.2×10^{-3}

Reaction of Oxygen Difluoride with Halogens.—Ruff and Menzel[3] found ClF to be a product of the reaction of OF_2 with **chlorine**. In the present work, a mixture of equal volumes of chlorine and oxygen difluoride exploded upon ignition by a spark to give ClF and oxygen.

When a mixture of three volumes of OF_2 with one of **Br_2** vapor was ignited by heat or a spark, oxygen was formed together with much BrF_3. By exploding a 5:1 mixture of OF_2 with Br_2, bromine pentafluoride was formed together with oxygen.

Iodine was found to react slowly at room temperature with oxygen difluoride to give iodine pentafluoride and a yellow solid. Numerous runs using a variety of procedures gave solids of various compositions IO_xF_y shown in Table II.

TABLE II

OBSERVED COMPOSITIONS OF IO_xF_y

Formed by reaction of I_2 in CCl_4 soln. with OF_2 gas		Formed by reaction of I_2 vapor with OF_2 gas	
x	y	x	y
0.78	1.43	0.96	1.61
0.66	1.43	1.07	1.48
0.80	1.68	1.01	1.49
0.83	1.58	1.98	0.37
1.31	1.31	1.79	0.35
		1.81	0.40

The yellow solid was substantially insoluble in liquid sulfur dioxide, trifluoroacetic acid, trifluoroacetic anhydride, or carbon tetrachloride. It reacted with water or hydrogen fluoride. No way was found to separate the solid into its components by the use of solvents.

At an elevated temperature iodine burned in oxygen difluoride, forming iodine pentafluoride and oxygen.

Iodine chloride, ICl, vapor reacted readily at room temperature with oxygen difluoride forming a yellow-orange smoke which settled out as a solid having the composition $IO_xF_yCl_z$ in which x, y, and z had the values indicated in Table III for various runs. The solid must have been a mixture. As in the case of the product from iodine, it was not found possible to separate the mixture into pure substances by using solvents.

TABLE III

PRODUCT FROM REACTION OF ICl WITH OF_2

x	y	z
1.16	1.49	0.54
0.82	1.20	1.21
1.38	0.52	0.87
1.32	0.90	0.17

Reaction with Sodium Thiocyanate.—Ruff and Menzel[3] found that OF_2 reacted with a solution of potassium thiocyanate to give a brick-red precipitate and other products. In this research as a stream of oxygen difluoride diluted with nitrogen was

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(1) Thesis of Robert A. Rhein, Order No. 63-4440, University Microfilms, Ann Arbor, Mich., 60 pp., microfilm copy $2.75, xerography copy $3.00, 1963.

(2) E. Simons, T. P. Wilson, and S. C. Schuman, *Natl. Nucl. En. Ser., Div. II*, **16**, 122 (1949).

(3) O. Ruff and W. Menzel, *Z. anorg. allgem. Chem.*, **198**, 39 (1931).

passed through a bed of pulverized sodium thiocyanate at room temperature the solid became brick-red in color. The product was extracted with water, leaving a red insoluble material having the properties of parathiocyanogen, $(CNS)_x$.

Reaction with Alkenes. Tetrafluoroethylene, oxygen difluoride, and nitrogen were introduced separately in the molar amounts, 0.0019, 0.0038, and 0.015, respectively, into a glass vessel cooled by liquid nitrogen. The vessel was then allowed to warm slowly to room temperature. As it did so, hexafluoroethane and carbonyl fluoride were formed. No pentafluoroethyl hypofluorite was found in the product.

A mixture of equal volumes of **ethylene** and oxygen difluoride at a total pressure of 100 mm. exploded after standing at room temperature for about 10 min. Other such mixtures at a total pressure of 60 mm. did not explode but instead reacted slowly giving fluoroethane and 1,2-difluoroethane. In two cases the product, when condensed, exploded after removal of unreacted oxygen difluoride.

1,2-Difluoroethane had strong absorption bands in the infrared at 3.40, 9.18, 9.40, 9.65, 9.70, and 11.16 (center of a triplet) μ. Medium bands occurred at 6.85, 7.20, 8.05, and 11.70 μ. In the mass spectrum "peaks" were found for the following ions in the order of decreasing abundance: CH_2F^+, $C_2H_3^+$, $C_2H_4^+$, $C_2H_3F^+$, $C_2H_2F^+$, $C_2H_2^+$, C_2H^+, CHF^+, CF^+, CH_2^+, $C_2H_4F_2^+$, $C_2H_4F^+$, $C_2H_3F_2^+$, C_2HF^+, $C_2H_2F_2^+$, C_2F^+, $C_2HF_2^+$, C_2^+, F^+, and CH^+.

Attempted Reaction with Dioxane in Water.—Since oxygen difluoride is somewhat soluble in water, it may very well behave as a fluorinating agent for various substances in aqueous solution. An unsuccessful attempt was made to replace the hydrogen atoms in dioxane by shaking a dilute aqueous solution of this substance in contact with gaseous oxygen difluoride at room temperature. No evidence was found for replacement of hydrogen atoms bound to carbon.

Other Reactions.—Oxygen difluoride reacted vigorously with ammonia, trimethylamine, or pyridine to give the acid fluoride of the base and a gas containing nitrous oxide. Hydrazine burst into flame upon contact with OF_2. With an aqueous solution of $N_2H_4 \cdot H_2SO_4$ or $NH_2OH \cdot H_2SO_4$ the reaction of OF_2 was slow, the gaseous product containing N_2 or N_2O, respectively. From tetrafluorohydrazine the product contained NO_2 and NF_3. Exploratory studies were made of the reaction of oxygen difluoride with C_2N_2, SO_2, or SOF_2.

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New Air-Stable Chromium(II) Compounds

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New chromium(II) compounds were prepared for use as convenient, air-stable materials for making chromium(II) electroplating baths.[1,2] These are Na_2CrF_4 and $CrXOH \cdot H_3BO_3$ (X = Cl, Br, I). Attempts to precipitate sodium analogs of $KCrF_3$ and $NH_4CrF_3 \cdot 2H_2O$[3] yielded no evidence for $NaCrF_3$, but resulted in the compound Na_2CrF_4. Attempts to prepare a "chromous borate"[4] by the reaction of a chromium(II) salt with an alkali borate resulted in a pyrophoric product. Modification of the pH to the range 2.9–4.0 before allowing chromium(II) chloride to react with boric acid led to $CrClOH \cdot H_3BO_3$. Bromine and iodine analogs of the last compound were made similarly.

Experimental

Sodium Fluorochromate(II), Na_2CrF_4.—A chromium(II) sulfamate solution was made by allowing 0.4 g.-atom of chromium powder to react with 0.4 mole of NH_2SO_3H in 200 ml. of water. The temperature was slowly raised to 90°. The bright blue solution was filtered to remove excess chromium and transferred to a flask containing 0.8 mole of NaF and 200 ml. of water. The mixture was stirred and heated to 80–100°, then allowed to cool. The precipitate was washed with 1:1 methanol–water, then with methanol, then dried. Deoxygenated water and nitrogen atmosphere were used throughout until the product was dry. The compound formed a mat of pale blue needles about 0.4 mm. long. The yield was about 75–78% based on Cr^{2+} and F^-. In other experiments a pure chromium(II) chloride solution formed the same product. Completeness of precipitation appeared to depend on a molal solubility product of the order of $[Na^+]^2[Cr^{2+}][F^-]^4 = 10^{-3}$ to 10^{-4}.

Anal. Calcd. for Na_2CrF_4: Na, 26.4; F, 43.7; Cr, 29.9. Found: Na, 27.8; F, 43.1; Cr (total), 29.5; Cr (divalent), 28.6.

Specific Properties.—The X-ray powder diffraction pattern was complex, with d = 4.86, 2.81, and 2.76 Å. as the strongest lines. The magnetic moment of Cr from magnetic susceptibility was about 5.2 B.M. Heating in air at 180° for 1 hr. caused less than 0.2% change in weight or titratable Cr^{2+} content.

$CrXOH \cdot H_3BO_3$ (X = Cl, Br, I).—$CrClOH \cdot H_3BO_3$ was made by pouring 1 l. of 1 M pure $CrCl_2$ soution into 500 ml. of water containing 1.5 moles of H_3BO_3, 0.57 mole of $CaCl_2 \cdot 2H_2O$, and 0.25 mole of $CaCO_3$. The mixture was held at 50° and stirred until gas evolution stopped, then was allowed to cool while stirring for 16 hr. The pale blue precipitate was filtered and washed by complete redispersion to a dilution ratio of $(5:1)^8$ with a 4.8% H_3BO_3 solution to prevent hydrolysis. It was dried under a high vacuum. The small amount of free boric acid left in it was calculated from the concentration in the wash solution and the weight of water trapped during drying. Air-free water and a nitrogen atmosphere were used throughout until after drying.

In other experiments, it was found necessary to hold the pH in the range 2.9–4.0 (as by the $CaCO_3$–Ca^{2+} buffer system) to avoid formation of air-oxidizable impurities. Similar Br and I compounds were formed, but of lower purity.

Anal. Calcd. for $CrClOH \cdot H_3BO_3$: H, 2.4; Cr, 31.3, Cl, 21.3; B, 6.5; Ca, 0. Found: H, 2.7; Cr, 31.2; Cl, 20.9; B, 7.1; Ca, 0.

Specific Properties.—$CrClOH \cdot H_3BO_3$ was a pale blue tetragonal crystalline powder. It showed a sharp X-ray powder diffraction pattern, indexed as tetragonal, $a_0 = 6.31$, $c_0 = 5.675$ Å. Density measurements in toluene showed 2.43 ± 0.03 g./cm.^{3}. From density and unit cell dimensions, the molecular weight of the unit cell was 331 ± 3 (double the formula weight is 332.6). The magnetic moment of Cr was found to be about 4.5 B.M.

General Properties.—All the compounds described were light or pale blue and remained so for over 2 years in unsealed laboratory containers. They could, however, be discolored toward green by access of very small amounts of air during any stage of preparation. Formation conditions indicate appreciable solubility in pure water, and this appeared to be so under the anaerobic conditions of preparation. However, after drying, they did not dissolve in pure water. It is possible that they may superficially oxidize in moist air. However, the chromium valence analysis increased on 2-year air exposure only from 2.03 to 2.18

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(1) A. J. Deyrup, U. S. Patent 2,996,353 (Aug. 15, 1961).

(2) A. J. Deyrup, U. S. Patent 3,088,801 (May 7, 1963).

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(4) A. Moberg, *J. prakt. Chem.*, (1) **44**, 332 (1848).