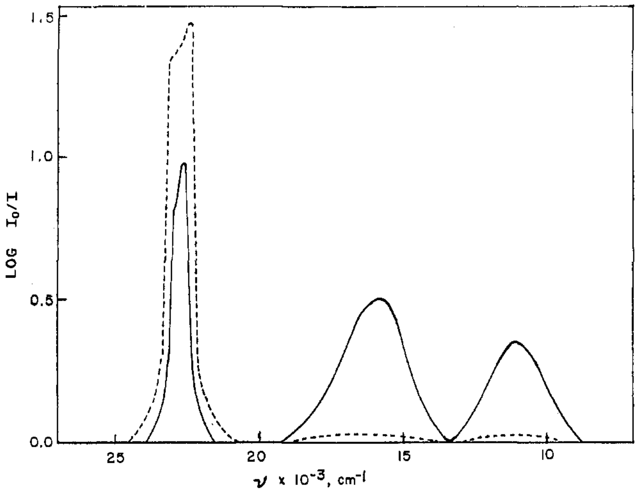

Fig. 1.—Polarized spectra of $(NH_4)_3Fe(C_3H_2O_4)_3$. The solid line is the σ polarization and the dashed line is the π polarization.

is less than half as large as that observed for the oxalato complex,[1] for which a greater trigonal distortion would not be unexpected. This observation is further supported by the spectra of $Cr(C_3H_2O_4)_3{}^{3-}$ (see below).

The Spectra of the Trismalonatochromate(III) Ion.—This research was initiated to study the differences that might be expected to exist in the spectral properties of malonato and oxalato complexes. A concerted effort was made to find a proper colorless host malonate complex for trivalent first transition series metal ions. This goal has not yet been achieved, but trismalonatochromate(III) ions have been introduced as impurities in the ammonium trismalonatoferrate(III) crystals and the polarized spectra recorded. After subtracting the spectrum for the iron complex, the results which are listed in Table I can be compared with those for the oxalato complex. Although the $^4A_2 \rightarrow {}^4T_1$ transition could not be observed because of intense bands in the iron compound, the close agreement of $\epsilon_\pi/\epsilon_\sigma$ of the low-energy band with that of the oxalato complex indicates that the $Cr(C_3H_2O_4)_3{}^{3-}$ ions occupy positions which are identical with those of the $Fe(C_3H_2O_4)_3{}^{3-}$ ions.

The trigonal splitting parameter, K, was estimated from the splitting of the $^4T_2$ level into $^4A_1$ and ^4E in the trigonal field and was found to be -120 cm.$^{-1}$. Although the magnitude of K so determined may not be very reliable, the sign of K is.[1,4] There are two possible contributions to an error in K. These are the uncertainty in the spectrum of $Fe(C_3H_2O_4)_3{}^{3-}$ which was subtracted from the spectrum of $Cr(C_3H_2O_4)_3{}^{3-}$ in the σ polarization and misalignment of the C_3 molecular axes in the crystal. Both of these would tend to decrease the absolute value of K. Piper and Carlin[5] have shown that the sign of K depends on the polar angle and thereby on the O–M–O angle within the chelate ring if the radial parameters are unchanged. Since there is little change in $10Dq$ in going from $Cr(C_2O_4)_3{}^{3-}$ to $Cr(C_3H_2O_4)_3{}^{3-}$, there is evidently little change in the radial parameters. The change in sign of K from 270 cm.$^{-1}$ for $Cr(C_2O_4)_3{}^{3-}$, which has an O–Cr–O angle of 83–85°, to -120 cm.$^{-1}$ for $Cr(C_3H_2O_4)_3{}^{3-}$ indicates that the O–Cr–O angle in the malonate chelate ring is slightly greater than 90°.

Acknowledgment.—The association of Professor T. S. Piper with this work is greatefully acknowledged.

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[5] T. S. Piper and R. L. Carlin, *ibid.*, **36**, 3330 (1962).

Contribution from The Inorganic Chemistry
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The Formation of Some Volatile Hydrides from Lower Oxides

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As part of a study of the chemistry of some lower oxides, samples of solid silicon monoxide were made by quenching the vapor over heated mixtures of silicon and silica. According to Erasmus and Personn[2] and Grube and Speidel,[3] quenched silicon monoxide, in contrast to material made by slower cooling from the vapor, is completely soluble in hydrofluoric acid. When the silicon monoxide made in this work was treated with 10% HF it dissolved completely with evolution of hydrogen and volatile silanes. This is thought to be the first report of this reaction of silicon monoxide.

The silicon monoxide was made by heating equimolar mixtures of finely divided 99.8% pure silicon and 99.7% pure silica under vacuum in an alumina tube furnace to 1350–1400°. The vapor was condensed on a water-cooled copper cold finger in the hot zone of the furnace. The monoxide was obtained as a brown-black solid, commonly in the form of needles oriented perpendicular to the cold finger surface. On exposure to air the solid frequently caught fire, and if allowed to oxidize more slowly it became a light brown color. No evidence of crystalline character could be obtained by X-ray diffraction studies on the solid.

Samples of 100–500 mg. of the solid were dissolved in 10% HF and the evolved silanes were trapped and separated gas chromatographically. Mono-, di-, tri-, iso- and *n*-tetra-, iso- and *n*-penta-, and iso- and *n*-hexasilane were identified from the mixture by their gas chromatographic retention times and in some cases by physical measurements. The same hydrides are formed by acid hydrolysis of magnesium silicide,[4] but the proportions of the different silanes are not exactly the same from the two sources. Table I shows

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[1] Address communications to this author at Department of Chemistry Rice University, Houston, Texas.

[2] H. deW. Erasmus and J. A. Personn, *J. Electrochem. Soc.*, **96**, 316 (1949).

[3] G. Grube and H. Speidel, *Z. Elektrochem.*, **53**, 339 (1949).

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TABLE I

COMPARISON OF RELATIVE AMOUNTS OF SILANES FROM Mg_2Si AND SiO

Silane yield ratio	SiO	Mg_2Si
Si_3H_8:n-Si_4H_{10}	2.3	2.8
n-Si_4H_{10}:n-Si_5H_{12}	2.2	3.0
n-Si_4H_{10}:i-Si_4H_{10}	8.0	13.8
n-Si_5H_{12}:i-Si_5H_{12}	2.5	2.8

the mean ratios of amounts of the silane isomers and homologs from magnesium silicide and from silicon monoxide (the ratios for magnesium silicide are little affected by the conditions under which it is prepared).

The total amount of silanes formed was determined by direct weighing of the volatiles. The theoretical yield was calculated by summing equations of the type

$$4SiO + 2H_2O = SiH_4 + 3SiO_2$$

$$(\text{or } 4SiO + 12HF = SiH_4 + 3SiF_4 + 4H_2O)$$

$$7SiO + 3H_2O = Si_2H_6 + 5SiO_2 \text{ etc.}$$

Knowing the relative yields of the different hydrides it was calculated that 160 g. of SiO (3.6 moles) should give 32 g. of mixed silanes (mean $SiH_{3.7}$). The experimental yields were variable, ranging from 9 to 24% of this theoretical yield. The cause of variability is uncertain but silicon monoxide samples giving high yields were found to be strongly adherent to the cold finger, *i.e.*, in good thermal contact with it.

The silicon monoxide was analyzed by reaction with alkali, by measuring the total gas evolution on dissolution in HF, and by the amount of silver formed on dissolving it in a solution of silver perchlorate in 20% HF.[5] The results all indicated an SiO content of 65–75%, *i.e.*, an Si : O ratio of 1 : 1.27 to 1 : 1.20 assuming that the rest is silica. It is not known if the apparent low purity was intrinsic or due to oxidative degradation before analysis as oxidation seemed rapid even with traces of oxygen present. However, it was found that the so-called Si_2O_3 made by Dadape and Margrave[6] also gave silanes with HF (the yield was 25–30% of theoretical, and the proportions of the different silanes were the same as from SiO), and it seems possible that if this species was present in the silicon monoxide it could account for the apparent high oxygen content and in part for silane evolution. The silicon monoxide samples contained 0.1–0.5% of HF involatile impurities. Analysis of these indicated that aluminum was the main metallic impurity in the monoxide; the magnesium content of the monoxide was below 0.02%.

Germanium monoxide prepared in a similar way from germania and germanium is almost insoluble in 10% HF. However, it was found that by condensing silicon monoxide and germanium monoxide together on the cold finger a black solid with a green sheen was obtained which gave silanes, silicon–germanium hydrides,[7,8] and germanes with 10% HF. A maximum of about 15% of the total volatiles were silicon–germanium hydrides (as $SiGeH_6$, Si_2GeH_8, Si_3GeH_{10}, Si_4GeH_{12}, with smaller amounts of $Si_2Ge_2H_{10}$ and $SiGe_2H_8$) with about 1% of germanes (as GeH_4, Ge_2H_6, and Ge_3H_8). If the germanium content of the solid was more than about 20% it was almost insoluble in the acid and gave only traces of hydrides.

Boron monoxide was also prepared in the same furnace system from boric oxide and boron.[9] The light brown condensates formed frequently exploded when scratched in air. They dissolved in water to give a solution which in 2 hr. evolved 0.3% of the boron as volatile boranes, and these were shown gas chromatographically to be mainly tetra- and pentaborane in a 5 : 1 mole ratio.

When hydrogen was passed over a mixture of silicon and silica at 1200° some monosilane was formed as has already been reported,[10] but the yields were tiny even with efficient quenching of the gases. A fibrous form of silica was deposited where the gas was quenched. Rapid cooling of the gases after passing hydrogen over heated boron and boric oxide[11] gave some diborane and also a white solid, probably boroxine $(HBO)_3$,[12] which evolved diborane together with tetra- and pentaborane on heating to 150°.

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CONTRIBUTION FROM THE
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Group VA and Group VIIA Oxofluorosulfates

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Some transition metal oxofluorosulfates have been prepared, *e.g.*, $MoO_2(SO_3F)_2$[1] and $CrO_2(SO_3F)_2$,[2] but no attempt has been made toward a systematic preparation and characterization of others of these transition metal compounds. A rewarding route is provided by the use of a transition metal or its anhydrous chloride in reaction with peroxodisulfuryl difluoride ($S_2O_6F_2$).

Experimental

Materials.—Peroxodisulfuryl difluoride was prepared by the catalytic fluorination of sulfur trioxide.[3] Niobium and rhenium metals were 99.9% pure. Anhydrous metal chlorides used were at least 99% pure. All other materials were of analytical reagent grade.

Analytical Methods.—Elemental analyses were obtained after basic hydrolysis in dilute sodium hydroxide. Sulfate was pre-

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