ometry measurements. At excess $NH_3OCH_3^+$ and excess Mn(III), no gaseous products were observed.

In the case of Ag(II), the first step is slower than the second, but it is considerably more rapid than the subsequent steps at $R < 1$. As R increases, the subsequent steps are complete within minutes. The oxidation of acetic and formic acids by silver(II) produces CO_2, with the initial step being rate determining.[13] The observed rate constants are almost three orders of magnitude less than k_{app} for the Ag(II)–$NH_3OCH_3^+$ system; the time scale for the reactions of acetic and formic acids is comparable to that for the complete oxidation of $NH_3OCH_3^+$.

The fact that the subsequent steps are much more rapid with Ag(II) than Mn(III) is not surprising, as k_{app} for Ag(II) is roughly three orders of magnitude greater than for Mn(III). The fact that, with Ag(II), the second step is much more rapid than the first at $R < 1$ is surprising. In the reaction with Mn(III), the radical $\cdot NHOCH_3$ was postulated as the first product (this species is consistent with the already mentioned pulse radiolysis study[18]); at $R < 1$, its dimerization was assumed to be much more rapid than its reaction with Mn(III). If $\cdot NHOCH_3$ is also the initial product in the reaction with Ag(II), further reaction of Ag(II) with $\cdot NHOCH_3$ or the postulated dimer, $N_2H_2(OCH_3)_2$, is extremely rapid. Since the dimer is probably relatively unreactive, it is likely that the Ag(II) + $\cdot NHOCH_3$ reaction competes favorably with the radical–radical dimerization itself. This difference in reactivity between Mn(III) and Ag(II) may be compared to the previously mentioned difference in the reactivity of Ce(IV) and Mn(III) with NH_3OH^+. For Ag(II), as for Mn(III), but not for Ce(IV), no gaseous products were observed.

The possibility of pathways involving Ag(III) being significant can be ruled out for both substrates. If Ag(III) were involved appreciably, a second-order dependence on [Ag(II)] and an inverse first-order dependence on [Ag(I)] would be expected.[11,19,20] The strong dependence of k_{app} on μ in the reaction of $NH_3OCH_3^+$ is interesting relative to the apparent insensitivity to this parameter in the reaction of NH_3OH^+. The source of this variation is unknown. The differences in reactivity of $NH_3OCH_3^+$ compared with other substrates with Mn(III) were also suggested as possibly being due to difficulties in coordination and H bonding of $NH_3OCH_3^+$ to Mn(III). The same may be the case with Ag(II), though at lower ionic strength the difference is not that great.

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(19) H. N. Po, J. H. Swinehart, and T. L. Allen, *Inorg. Chem.*, **7**, 244 (1968).

(20) See J. Pumies, W. Roebke, and A. Henglein, *Ber. Bunsenges. Phys. Chem.*, **72**, 844 (1968), and B. M. Gordon and A. C. Wahl, *J. Amer. Chem. Soc.*, **80**, 273 (1958), for the rate of 2Ag(II) → Ag(III) + Ag(I).

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Xenon(II) Difluorophosphates. Preparation, Properties, and Evidence for the Difluorophosphate Free Radical

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Received May 26, 1971

Xenon(II) fluoride difluorophosphate, $FXeOPOF_2$, and xenon(II) bis(difluorophosphate), $Xe(OPOF_2)_2$, are obtained in high yield by reactions of xenon difluoride with μ-oxo-bis(phosphoryl difluoride), $P_2O_3F_4$, at 22° in trichlorofluoromethane. The new compounds are pale yellow solids which decompose readily at 22° forming an unstable material, which is probably the difluorophosphate free radical.

Introduction

Several new xenon compounds have recently been prepared by reactions of the xenon fluorides with strong oxy acids.[1-5] Xenon fluorosulfates, perchlorates, trifluoroacetates, pentafluorotellurates, and possibly nitrates have been obtained by this method. All of these compounds have been obtained with XeF_2 and both the mono- and bis-substituted derivatives have been prepared. No xenon(IV) and one xenon(VI) fluorosulfate have been synthesized to date from XeF_4 and XeF_6. Attempts to extend this method of preparation to the synthesis of xenon(II) difluorophosphates using difluorophosphoric acid have been unsuccessful, because of side reactions involving fluorination of phosphorus. We have now obtained both $FXeOPOF_2$ and $Xe(OPOF_2)_2$ by the reaction of XeF_2 with pure $P_2O_3F_4$ in CCl_3F. The compounds have only limited stability at 22° similar to the isoelectronic xenon(II) fluorosulfates, but unlike the lattter they do not yield a stable peroxide on decomposition.

Experimental Section

General Data.—Manipulations of volatile compounds were carried out in a Monel–Kel-F vacuum system or a glass system equipped with glass–Teflon valves. Pressures were measured with a Barton 316SS bellows gauge in the metal system and a mercury manometer in the glass system. Kel-F No. 3 polymer oil was used to protect the mercury. Amounts of volatile materials were determined by PVT measurements or by weight. Xenon and oxygen were identified by their physical properties

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(1) M. Eisenberg and D. D. DesMarteau, submitted for publication in *Inorg. Chem.*

(2) N. Bartlett, M. Wechsberg, F. O. Sladky, P. A. Bulliner, G. R. Jones, and R. D. Burbank, *Chem. Commun.*, 703 (1969).

(3) F. Sladky, *Angew. Chem.*, **81**, 536 (1969).

(4) F. Sladky, *ibid.*, **81**, 330 (1969).

(5) D. D. DesMarteau and M. Eisenberg, submitted for publication in *Inorg. Chem.*

TABLE I

REACTIONS OF XeF_2 WITH $P_2O_3F_4$

Reactants[a]			
XeF_2	$P_2O_3F_4$	Conditions	Products[a]
0.66	0.64	CCl_3F, −22°, 4 days	$FXeOPOF_2$, 0.41; POF_3, 0.84; Xe, 0.20; O_2, 0.10
0.64	1.31	CCl_3F, −22°, 5 days	$Xe(OPOF_2)_2$, 0.57; POF_3, 1.30; Xe, 0.04; O_2, 0.02; $P_2O_3F_4$, 0.07
0.40	0.40	POF_3, −37°, 1.5 days	$FXeOPOF_2$, 0.21; POF_3, 0.60; Xe, 0.17; O_2, 0.04
1.36	1.35	−20 to −5°, 2 days	$FXeOPOF_2$, 0.65; POF_3, 2.18; Xe, 0.74; O_2, 0.38
0.53	1.06	−20 to −9°, 1.5 days	$Xe(OPOF_2)_2$, 0.29; Xe, 0.23; O_2, 0.11; POF_3–$P_2O_3F_4$, 0.15 g

[a] Millimoles.

and other known compounds by their infrared spectra. In each case comparison was made with pure samples run under identical conditions.

Infrared spectra were taken on a Beckman IR-10 using a 10-cm Monel or glass cell fitted with silver chloride windows. Raman spectra were recorded on a Spex 4001 argon laser instrument employing the 5145-Å line for excitation. Samples were contained in sealed $^1/_8$-in. o.d. Kel-F tubes.

Ultraviolet spectra were recorded on a Beckman DK-1 or a Cary 14 spectrophotometer. The solutions in CCl_4 were held in 1-cm quartz cells. Electron spin resonance spectra were taken on a Varian E-9 EPR spectrometer using CCl_4 as a solvent.[6]

Reagents.—Xenon difluoride was prepared by the photochemical reaction of excess Xe with F_2.[7] Samples were purified in a Kel-F system by sublimation and stored in Kel-F containers. μ-Oxo-bis(phosphoryl difluoride) was prepared by the photolysis of POF_2Br and O_2.[8] To ensure purity, $P_2O_3F_4$ was prepared as needed and used immediately. Solvents were dried over P_4O_{10} and transferred under vacuum. Spectral grade quality CCl_4 was used in the uv and esr measurements.

Reactions of XeF_2 with $P_2F_3O_4$.—The reactions between XeF_2 and $P_2O_3F_4$ were carried out in 6-ml Kel-F reactors fitted with a 316SS valve. The general procedure was to condense $P_2O_3F_4$ onto XeF_2 held at −196°. The solvent (2 ml) was then added and the reactor was warmed to the desired temperature. After reaction was complete, the vessel was cooled to −196° and O_2 was removed. The amount of O_2 was measured by expansion of the gas into a calibrated volume and observing the pressure and temperature. Xenon was removed at −131° and measured in the same way as O_2, followed by the solvent and POF_3. The amount of POF_3 was determined by the difference in the weight of the solvent added and the weight of the volatile material removed at −50°. After removing the solvent and POF_3 the vessel was pumped on at 0° to check for $P_2O_3F_4$. The infrared spectrum of the O_2 and Xe, taken at a pressure of 30 mm or greater, showed no detectable absorptions above background. Similar spectra of the POF_3–CCl_3F mixture showed no peaks that could be attributed to other products. The infrared spectrum of $P_2O_3F_4$, when present, usually showed the presence of small amounts of $HOPOF_2$ and POF_3.

During the course of all $P_2O_3F_4$–XeF_2 reactions, an orange color developed on the solid and in the $CFCl_3$ solvent. Small amounts of an orange material were observed in the POF_3–$CFCl_3$ mixture removed at −50° and in the material removed from the xenon difluorophosphate at 0° and the solid xenon difluorophosphate usually had an orange coloration after removing all volatile material up to 0°. In all cases the orange color disappeared rapidly when warmed to 22°. None of the material could be isolated from the preparation, but a small amount was isolated from the decomposition of $Xe(OPOF_2)_2$ described in the next section. The same orange color also developed in reactions with $HOPOF_2$ at temperatures below −50°. In the presence of the acid, this substance was considerably less stable as the orange color could not be observed much above −50°. The data for some representative runs are summarized in Table I.

Decomposition of Xenon Difluorophosphates.—The decomposition of $FXeOPOF_2$ and $Xe(OPOF_2)_2$ were studied both in a static system and by pumping on the compounds through a cold trap. In the static system (mmol) $XePOF_2$ (0.39) and $Xe(OPOF_2)_2$ (0.52) were allowed to stand in 6-ml Kel-F vessels at 22° until all the solid had disappeared. The products were then separated and identified as described in the previous section. The products were (mmol) Xe (0.31), O_2 (0.16), and POF_3 (0.35) with $FXeOPOF_2$ and Xe (0.59), O_2 (0.25), and $P_2O_3F_4$ (0.98) with $Xe(OPOF_2)_2$.

The decomposition products observed with $Xe(OPOF_2)_2$ while pumping on the compound at 22° through a −196° trap were the same as above (O_2 was not collected). With FXeOPOF, XeF_2 along with smaller amounts of Xe and POF_3 collected at −196°. After all the xenon had evolved, a white powder corresponding to $(PO_2F)_n$ remained in the vessel. When this solid was allowed to react with a stoichiometric amount of XeF_2 at 22°, Xe, POF_3, and O_2 were formed exothermically. These observations suggest at least a two-step decomposition of $FXeOPOF_2$ in the static system with XeF_2 and $(PO_2F)_n$ as intermediate products.

The −196° trap in these decompositions also contained small amounts of an orange solid which disappeared rapidly on warming. A small amount (*ca.* 10 mg) of the solid was isolated in one decomposition of $Xe(OPOF)_2$. This was achieved by first removing the Xe at −131° from the −196° trap and then collecting the material volatile at −78° by pumping through a −196° Kel-F trap. The small amount of orange solid collected in this way melted to a red liquid and vaporized to yellow gas. The color changes were reversible but the colors slowly faded at 22° and on cooling a colorless liquid and white solid could be observed after about 30 min. After the color had almost completely faded, the infrared spectrum showed the presence of $P_2O_3F_4$ with traces of $HOPOF_2$ and POF_3. A noncondensable gas at −196° was also present suggesting the following reaction had occurred: $2PO_2F_2 \rightarrow P_2O_3F_4 + {}^1/_2O_2$. The intense colors observed for this material from −196 to 22° suggest that if the color is due to the presence of a free radical, the extent of dimerization is small even at −196°.

Results

Xenon difluoride and $P_2O_3F_4$ react at low temperature to give the new compounds $FXeOPOF_2$ and $Xe(OPOF_2)_2$. The best yields are obtained in CCl_3F at −22°. The reactions follow the equations

$$XeF_2 + P_2O_3F_4 \longrightarrow FXeOPOF_2 + POF_3$$
$$XeF_2 + 2P_2O_3F_4 \longrightarrow Xe(OPOF_2)_2 + 2POF_3$$

The compounds are pale yellow solids which decompose in a few days at 22° according to the equations

$$FXeOPOF_2 \longrightarrow XeF_2 + (PO_2F)_n \longrightarrow Xe + {}^1/_2O_2 + POF_3$$
$$Xe(OPOF_2) \longrightarrow Xe + {}^1/_2O_2 + P_2O_3F_4$$

The Raman spectra of the solids are given in Table II. Both show considerable similarity to each other and to previously reported spectra for alkali metal and transition metal difluorophosphates.[9–11] Attempts to

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(6) The authors thank Dr. S. Chatterjee of Air Force Cambridge Research Laboratory, Bedford, Mass., for the esr spectra.

(7) J. H. Holloway, *J. Chem. Educ.*, **43**, 202 (1966).

(8) P. A. Bernstein, F. A. Hohorst, M. Eisenberg, and D. D. DesMarteau, *Inorg. Chem.*, **10**, 1549 (1971).

(9) R. C. Thompson and W. Reed, *Inorg. Nucl. Chem. Lett.*, **5**, 581 (1969).

(10) J. Weidlein, *Z. Anorg. Allg. Chem.*, **358**, 13 (1968).

(11) K. Buhler and W. Bues, *ibid.*, **308**, 62 (1961).

TABLE II

RAMAN DATA

$FXeOPOF_2$	$Xe(OPOF_2)_2$	Assignment
1295 m	1299 w	$\nu_{as}(PO_2)$
1200 m		
1125 m	1123 m	$\nu_s(PO_2)$
950 w, br	970 w, br	$\nu_{as}(PF_2)$
?	890 w	$\nu_s(PF_2)$
668 m	675 m	PO_2F_2 def and XeO, XeF str
640 m	560 s	
560 m	525 m	
485 w	510 w	
445 s	456 m	
395 m		

obtain infrared spectra of the solids on AgCl windows resulted in reaction with the windows. The observed ir spectrum was identical with that of $AgOPOF_2$.[12]

During the preparation of the xenon difluorophosphates, an intense orange color develops on the surface of the solid and the solvent becomes yellow. The orange coloration of the solid disappears rapidly on warming to 22° but the yellow solution remains colored for several hours. A yellow solution also results if the pale yellow xenon difluorophosphates are allowed to stand in contact with liquid CCl_4 or $CFCl_3$. The compounds themselves have very little apparent solubility in either liquid. The color is due to a free radical which is apparently formed from the decomposition of both $FXeOPOF_2$ and $Xe(OPOF_2)_2$.

The uv spectrum of a yellow CCl_4 solution formed from $Xe(OPOF_2)_2$ at 22° is shown in Figure 1. The vibrational progression is centered at 345 nm and calculation shows that the spacings are regular at 650 cm^{-1}. The intensity of the uv absorption was proportional to the intensity of the orange color in the solutions. As the orange color faded with time, the 345-nm absorption also decreased. The esr spectrum of the same solution is shown in Figure 2. The broad line could not be resolved further at 22°. The line width is 67 G with a g value of 2.0067.

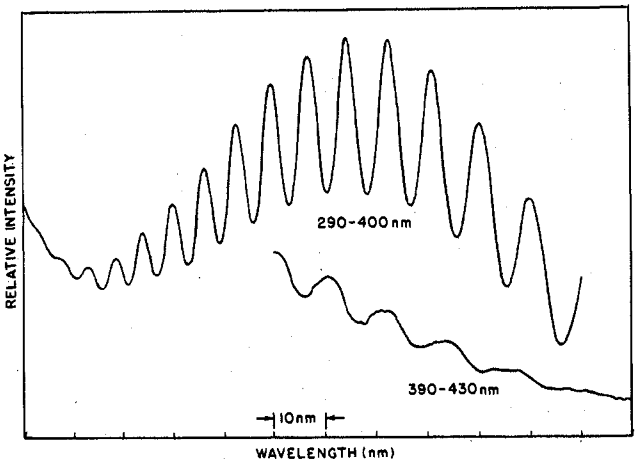

Figure 1.—Absorption spectrum of a yellow CCl_4 solution formed by $Xe(OPOF_2)_2$ at 22°. The spectrum is shown from 290 to 430 nm with a source change at 390 nm.

Discussion

In the course of the study of the reactions of XeF_2 with strong oxy acids, we investigated the reaction of XeF_2 with $HOPOF_2$. Our goal was to prepare a xenon difluorophosphate as indicated in the equation

$$XeF_2 + nHOPOF_2 \longrightarrow F_{2-n}Xe(OPOF_2)_n + nHF \quad (n = 1, 2)$$

These reactions resulted in many products but no isolable xenon difluorophosphate. Under a variety of experimental conditions, the product were always Xe, O_2, HF, POF_3, and PF_5. Since XeF_2 in the presence of HF is a powerful fluorinating reagent,[13] the failure to obtain the desired xenon compound was attributed to this.

We then decided to add $P_2O_3F_4$ to the reactants to scavenge the HF by the reaction $HF + P_2O_3F_4 \rightarrow HOPOF_2 + POF_3$. This was partially successful as small amounts of the xenon difluorophosphates were obtained. Phosphorus pentafluoride was still a major product, however, and as the ratio of $P_2O_3F_4:HOPOF_2$ was increased, the amount of PF_5 decreased. This suggested that pure $P_2O_3F_4$ might react to give the desired product. The preparation of pure $P_2O_3F_4$ by photolysis of POF_2Br with O_2 was developed to carry out the reaction.[8]

When anhydrous $P_2O_3F_4$ is allowed to react with XeF_2, no PF_5 is observed and good yields of the xenon compounds are obtained. The anhydride melts at 0°, and at a temperature near the melting point, the reaction is difficult to control. At temperatures significantly below the melting point, the solid–solid reaction is very slow and complete reaction is difficult to achieve. Trichlorofluoromethane and POF_3 were tried as solvents to facilitate reaction between $P_2O_3F_4$ and XeF_2 at lower temperatures. Both were satisfactory but $CFCl_3$ is much more convenient experimentally. As shown in Table I, yields as high as 90% can be obtained in $CFCl_3$.

The Raman spectra of $FXeOPOF_2$ and $Xe(OPOF_2)_2$ are consistent with the presence of a difluorophosphate group but we were unable to obtain high-quality spectra necessary for definitive assignments. The observed frequencies in 1100–1300-cm^{-1} region are most readily assigned to $\nu_s(PO_2)$ and $\nu_{as}(PO_2)$ stretches consistent with the presence of $PO_2F_2^-$ or perhaps bidentate PO_2F_2, where the solids could be polymeric through oxygen bridge bonds.

Assignments of the other observed Raman frequencies are difficult because the Xe–F and Xe–O stretches probably occur at about 600 cm^{-1} and below. This region is also characteristic for the deformation modes of the PO_2F_2 group and no positive assignments can be made without further work.

The decomposition of the xenon difluorophosphates is interesting because of the formation of a moderately stable free radical. The radical species is probably

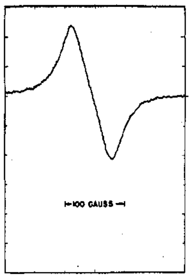

Figure 2.—Esr spectrum of a yellow CCl_4 solution formed by $Xe(OPOF_2)_2$ at 22°.

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[12] P. A. Bernstein and D. D. DesMarteau, unpublished results.

[13] N. Bartlett and F. O. Sladky, *Chem. Commun.*, 1046 (1968).

PO_2F_2 based on a comparison of the uv and esr spectra with the isoelectronic fluorosulfate free radical SO_3F.[14–17] The latter exhibits a complex uv absorption in the gas phase and its esr spectrum is a single broad line in both the liquid and gas phases. The failure to observe the fluorine hyperfine interaction in SO_3F is attributed to the large magnitude of the line width.[16] A similar argument can be made for the failure to observe the phosphorus and fluorine hyperfine interaction in PO_2F_2.

Other evidence strongly supports the formation of the PO_2F_2 radical in these systems. The persistent orange color observed in the reactions of XeF_2 with $HOPOF_2$ and $P_2O_3F_4$ and the isolation of a small amount of the orange material from the decomposition of $Xe(OPOF_2)_2$ are consistent with the formation of a reactive free radical. The apparent instability of PO_2F_2 in the presence of $HOPOF_2$ is also consistent with the failure to observe the radical by electrolysis of $HOPOF_2$.[18]

The formation of a PO_2F_2 free radical from the decomposition of $FXeOPOF_2$ and $Xe(OPOF_2)_2$ is quite reasonable based on the behavior of the xenon fluorosulfates. All of these including $FXeOSO_2F$,[2] $Xe(OSO_2F)_2$,[1,2] and F_5XeOSO_2F[5] form the peroxide $S_2O_6F_2$[19] on decomposition. These reactions probably involve an intermediate SO_3F radical. The difference between the xenon(II) difluorophosphates and fluorosulfates is that the dimer is stable in the latter case whereas PO_2F_2 is unstable and may be formed only as a minor decomposition product.

Acknowledgment.—This work was supported by National Science Foundation Grant No. GP23098. We wish to thank Professor C. H. Perry for the use of his Raman spectrometer.

(14) F. B. Dudley and G. H. Cady, *J. Amer. Chem. Soc.*, **85**, 3375 (1963).

(15) F. Neumayer and N. Vanderkooi, Jr., *Inorg. Chem.*, **4**, 1234 (1965).

(16) P. M. Nutkowitz and G. Vincow, *J. Amer. Chem. Soc.*, **91**, 5956 (1969).

(17) R. A. Stewart, S. Fujiwara, and F. Aubke, *J. Chem. Phys.*, **48**, 5524 (1968).

(18) D. D. DesMarteau, Ph.D. Thesis, University of Washington, 1966.

(19) F. B. Dudley and G. H. Cady, *J. Amer. Chem. Soc.*, **79**, 513 (1957).

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Potassium, Rubidium, Cesium, and Barium Ferrates(VI). Preparations, Infrared Spectra, and Magnetic Susceptibilities

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Received December 2, 1971

Potassium, rubidium, and cesium ferrates(VI) have been prepared in high purity and good yield using the corresponding hypochlorite as the oxidizing agent and the corresponding hydroxide as the precipitation medium. Pure barium ferrate(VI) has been prepared by precipitation from a carbonate-free potassium ferrate(VI) solution. Potassium, rubidium, and cesium ferrates(VI) are all isostructural with β-potassium sulfate. The space group is *Pnma* and there are four molecules in the orthorhombic unit cell. The unit cell dimensions are $a = 0.7705$ nm, $b = 0.5863$ nm, $c = 1.0360$ nm for potassium ferrate(VI); $a = 0.8040$ nm, $b = 0.6052$ nm, $c = 1.0665$ nm for rubidium ferrate(VI); and $a = 0.8434$ nm, $b = 0.6289$ nm, $c = 1.1127$ nm for cesium ferrate(VI). The infrared spectra of the four ferrates(VI) have been measured. The temperature-dependent magnetic susceptibility measurements were obtained using the Faraday method over a temperature range of 85–303°K. The magnetic susceptibilities of the four ferrates(VI) were found to obey the Curie–Weiss law and to be field independent. Effective magnetic moments from the Curie–Weiss law were found to be $2.79\ (\pm 0.03) \times 10^{-23}\ \mathrm{A\ m^2}$, $2.70\ (\pm 0.03) \times 10^{-23}\ \mathrm{A\ m^2}$, $2.67\ (\pm 0.03) \times 10^{-23}\ \mathrm{A\ m^2}$, and $2.92\ (\pm 0.03) \times 10^{-23}\ \mathrm{A\ m^2}$ for potassium, rubidium, cesium, and barium ferrates(VI), respectively.

Introduction

The preparations of potassium ferrate(VI)[2–5] and barium ferrate(VI)[6–8] are well known. A simple procedure to obtain high-purity rubidium and cesium ferrate(VI)[9] has not, however, been previously reported. A general method for the preparation of the potassium, rubidium, and cesium salts is given below, along with the method used to obtain the barium salt.

The crystal system of K_2FeO_4[8,10] has been known for some time and the infrared spectra of Na_2FeO_4, K_2FeO_4, $SrFeO_4$, and $BaFeO_4$[11–14] have been previously reported. The magnetic susceptibilities of K_2FeO_4 and Cs_2FeO_4[2,15] have been determined by the Gouy method on samples containing ferric hydroxide impurities. The magnetic susceptibilities of K_2FeO_4, $SrFeO_4$, and $BaFeO_4$[16] have recently been determined using a torsion balance magnetometer. However, infrared spectra and adequate temperature-dependent magnetic

(1) Holder of a National Research Council of Canada Studentship for 1967–1971.

(2) H. J. Hrostowski and A. B. Scott, *J. Chem. Phys.*, **18**, 105 (1950).

(3) G. W. Thompson, L. T. Ockerman, and J. M. Schreyer, *J. Amer. Chem. Soc.*, **73**, 1379 (1951).

(4) J. Tousěk and A. Toušková, *Chem. Zvesti*, **11**, 113 (1957).

(5) J. T. Riley, Ph.D. Thesis, *Diss. Abstr. B*, **30**, 1547 (1969).

(6) J. R. Gump, W. F. Wagner, and J. M. Schreyer, *Anal. Chem.*, **26**, 1957 (1954).

(7) V. R. Scholder, H. von Bunsen, F. Kindervater, and W. Zeiss, *Z. Anorg. Allg. Chem.*, **282**, 268 (1955).

(8) B. Helferich and K. Lang, *ibid.*, **263**, 169 (1950).

(9) J. R. Gump and W. F. Wagner, *Trans. Ky. Acad. Sci.*, **15**, 112 (1954).

(10) H. Krebs, *Z. Anorg. Allg. Chem.*, **263**, 175 (1950).

(11) N. Becarud and C. Dural, *C. R. Acad. Sci.*, **257**, 1930 (1963).

(12) P. Tarte and G. Nizet, *Spectrochim. Acta*, **20**, 503 (1964).

(13) N. Becarud, Commissariat à l'Energie Atomique France Rapport No. 2895, Paris, 1966.

(14) W. P. Griffith, *J. Chem. Soc. A.*, 1467 (1966).

(15) W. Klemm, C. Brendel, and G. Wehrmeyer, *Chem. Ber.*, **93**, 1506 (1960).

(16) T. Shinjo, T. Ichida, and T. Takada, *J. Phys. Soc. Jap.*, **29**, 111 (1970).