

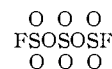
compound. Perfluorocyclopentane was used as a reference material with a field strength of 15,020 gauss. The $S_2O_5F_2$ showed a single peak at a negative shift of 31.7 p.p.m. from the reference sample. Comparison of areas under the curves corrected for different densities gave approximately a 5:1 ratio for the number of fluorine atoms per molecule. These data show that the compound $S_2O_5F_2$ has two fluorine atoms per molecule, both having the same chemical environment.

Mass Spectra.—Mass spectra were obtained with a Consolidated Electrodynamics Corp. Mass Spectrometer, Model 21-103C with an ionizing current of 10.5 μ amp, and an ionizing potential at 70 volts. The butane sensitivity was 27.7 divisions per micron. Spectra were obtained for $S_2O_5F_2$ as well as for $S_2O_3F_2$ and $S_2O_6F_2$ for comparison. The $S_2O_5F_2$ spectrum showed major peaks corresponding to SO_2F^+ , SOF^+ , SO_2^+ , SO_3^+ and numerous minor peaks. The parent peak at mass number 262 was missing in all spectra. Persistent peaks at mass numbers 182 and 184 corresponding to $S_2O_5F_2^+$ could not be explained, comparison with the spectrum of $S_2O_3F_2$, showed marked similarities even though all other tests showed the absence of $S_2O_3F_2$ in the $S_2O_5F_2$ sample. It is probable, therefore, that the $S_2O_5F_2$ molecule is extensively disintegrated in the mass spectrometer or in the line for admitting the gas to the spectrometer, with the production of $S_2O_3F_2$.

Preparation from SO_3 and BF_3 .—Following the method of Lehmann and Kolditz⁹ a compound was isolated which had a molecular weight of 267 as determined by gas density. The

melting point, infrared spectrum and mass spectrum were identical with those found for the product obtained from the reaction of sulfur dioxide with peroxydisulfuryl difluoride. A second product of this reaction was identified as pyrosulfuryl fluoride, $S_2O_5F_2$.

Structure.—From the fact that one mole of $S_2O_5F_2$ reacts with a solution of potassium hydroxide to give approximately two moles of SO_3F^- and one of SO_4^{--} , Lehmann and Kolditz proposed the structure



This structure is consistent with the nuclear magnetic resonance spectrum which indicates only one type of fluorine atom, but it is not consistent with a mass spectrum containing a $S_2O_5F_2^+$ peak. The writers are of the opinion that the above structure is correct and that the $S_2O_5F_2^+$ peak in the mass spectrum is probably due to $S_2O_3F_2$ as indicated earlier.

The name trisulfuryl fluoride was assigned to $S_2O_3F_2$ by the discoverers. If the above structure is correct the name sulfuryl fluorosulfonate is equally good.

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SEATTLE, WASHINGTON
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[CONTRIBUTION FROM THE NATIONAL LEAD COMPANY OF OHIO]

Evidence for the Existence of Peroxyuranic Acid¹

By R. E. DEMARCO, D. E. RICHARDS, T. J. COLLOPY AND R. C. ABBOTT

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Uranium trioxide was treated with aqueous hydrogen peroxide to form a hydrated uranium peroxide compound identical to that precipitated from aqueous uranyl nitrate solution by the addition of hydrogen peroxide. The stoichiometric compound, $UO_4 \cdot 2H_2O$, was shown to react with alcoholic potassium hydroxide to form hydrated monobasic ($KHUO_5 \cdot xH_2O$) and dibasic ($K_2UO_6 \cdot xH_2O$) potassium salts. A hydrated peroxyuranic acid structure ($H_2UO_5 \cdot H_2O$) was concluded to best represent a compound of the stoichiometry $UO_4 \cdot 2H_2O$. This structure was supported by the infrared absorption spectrum and reactions with a strong base of the uranium peroxide compound.

Introduction

Since Fairley² first prepared hydrated uranium peroxide by the precipitation of uranium from weakly acidic aqueous solutions of uranyl nitrate or uranyl acetate with hydrogen peroxide, a controversy has existed regarding its structure. Despite the controversy regarding its structure, the stoichiometric compound $UO_4 \cdot 2H_2O$ readily can be prepared with a high degree of purity.

Previous experimental efforts to define the structure of this uranium peroxide compound were based on its reactions in aqueous solution, its stepwise thermal decomposition to U_3O_8 and/or infrared spectral studies. As a result of these experiments the following structures have been postulated for the compounds: $UO_4 \cdot 2H_2O$,³ $UO_2(O_2) \cdot 2H_2O$,⁴ $UO_3 \cdot H_2O_2 \cdot H_2O$,⁵ $H_2UO_5 \cdot H_2O$ ⁶ and H_4UO_6 .⁷

(1) This paper is based on work performed for the Atomic Energy Commission by the National Lead Company of Ohio at Cincinnati, Ohio.

(2) T. Fairley, *Chem. News*, **33**, 237 (1876).

(3) A. Rosenheim and H. Daehr, *Z. anorg. allgem. Chem.*, **181**, 177 (1929).

(4) G. Tridot, *Compt. rend.*, **232**, 1215 (1951).

(5) G. F. Hüttig and E. v. Schroeder, *Z. anorg. allgem. Chem.*, **121**, 243 (1922).

(6) A. Sieverts and E. L. Müller, *ibid.*, **173**, 297 (1928).

(7) J. J. Katz and E. Rabinowitch, "The Chemistry of Uranium," McGraw-Hill Book Co., Inc., New York, N. Y., 1951, pp. 245-246.

In light of the recent work by Gentile, Talley and Collopy,⁸ further substantiating the acidic character of hydrated uranium trioxide by its reaction with the weak base urea to form urea uranate, additional study of the reactions of the peroxy-uranium hydrate compounds was warranted.

Preliminary tests employing uranium peroxide hydrates and aqueous or alcoholic solutions of urea failed to produce sufficient quantities of a compound corresponding to urea peroxyuranate. A solid material corresponding to urea peroxyuranate was precipitated, however, from a concentrated solution of diaquotetraureadioxouranium-(VI) nitrate by the addition of hydrogen peroxide. This precipitate, after continued contact with water, hydrolyzed to a peroxyuranic acid hydrate.

In view of the above results and the generally diminished acidity of peroxyacids as compared with fundamental oxygen acids of the same system, a series of tests was conducted with the strong base potassium hydroxide in alcoholic media to demonstrate the acidic character of uranium peroxide hydrates. These experiments were supplemented with infrared spectral data to determine the presence of the uranyl group, hydrate water and hydroxyl groups. X-Ray diffraction patterns were

(8) P. S. Gentile, L. H. Talley and T. J. Collopy, *J. Inorg. Nuclear Chem.*, **10**, 114 (1959).

obtained to verify the existence of a single homogeneous product phase.

Experimental

Materials.—1. The hydrated uranium peroxide compound was precipitated from an aqueous solution of uranyl nitrate hexahydrate (Reagent Grade purchased from Baker Chemical Company) using the procedure described by Watt, Achorn and Marley.⁹ The resulting precipitate was filtered, washed with distilled water and then alcohol, prior to drying at 100° for 60 minutes.

Calcd. for $H_2UO_5 \cdot H_2O$: U, 70.41; peroxy oxygen, 9.46. Found: U, 70.29 \pm 0.07; peroxy oxygen, 9.41 \pm 0.11.

2. The brick-red X-ray amorphous form of uranium trioxide, prepared by the thermal decomposition of $UO_3 \cdot 2H_2O$ (Calcd. U, 73.91. Found: U, 73.90 \pm 0.07) at 400° was slurried with an excess of aqueous 15% H_2O_2 solution at room temperature for 20 hr. The product of this slurry was filtered, washed with distilled water and then alcohol, prior to drying at 100° for 60 minutes.

Calcd. for $H_2UO_5 \cdot H_2O$: U, 70.41; peroxy oxygen, 9.46. Found U, 70.20 \pm 0.07, peroxy oxygen, 9.44 \pm 0.11.

Analytical Methods.—Uranium, potassium and peroxy oxygen were determined in accordance with the procedures given by "Scott's Standard Methods of Chemical Analysis."¹⁰

Uranium was determined (1) gravimetrically by ignition to U_3O_8 or (2) volumetrically by titration with standard 0.1 *N* potassium permanganate. The volumetric method of analysis was used for all potassium containing samples.

Potassium was determined gravimetrically by precipitation as potassium perchlorate from an ethyl alcohol-butyl acetate solution.

Peroxy oxygen was determined by dissolution of the sample in dilute sulfuric acid and titration with standard 0.1 *N* potassium permanganate.

Water was determined by titration of methyl alcohol slurries of the sample with Karl Fischer reagent.¹¹

Infrared spectra were obtained with a Beckman Model IR-4 spectrometer using potassium bromide pellets containing 1 w/o sample.^{12,13}

X-Ray powder diffraction patterns were obtained at room temperature with a Norelco X-ray diffraction unit using 114.7 mm. cameras and unresolved $Cu K\alpha_1$ - α_2 radiation.

Procedure.—Five-gram samples of the hydrated uranium peroxide compound (preparations I and II) were treated with 200 ml. of an alcohol solution of carbonate-free potassium hydroxide ranging in strength from 0.02 to 4.0 molar. The reaction was allowed to proceed, at room temperature with vigorous stirring, for 24 hr. before the product was filtered, alcohol-washed free of excess base and air-dried to a constant weight.

Results and Discussion

Infrared spectra and X-ray diffraction patterns of the two uranium peroxide starting compounds were obtained. The infrared spectra and diffraction patterns of these materials were not affected by the mode of preparation. Strong infrared absorption bands were found at 2.94, 3.20, 6.18, 10.65 and 11.05 μ ; a shoulder occurred at 11.55 μ .

The absorption band at 10.65 μ and the shoulder at 11.55 μ previously have been associated with the asymmetric and symmetric vibrations of the uranyl group.^{14,15} The band at 6.18 μ is due to the presence

of hydrate water¹⁶ in the starting peroxide compound. The broad infrared absorption band with maxima at 2.94 and 3.20 μ is indicative of the presence of hydrogen-bonded hydroxyl groups. The remaining absorption band at 11.05 μ may be attributed to the asymmetric vibration of a uranyl group, one oxygen of which is hydrogen bonded to a water molecule. Hydrogen bonding to the oxygen of a $M=O$ group usually results in a frequency shift similar in direction and magnitude to the 30 cm^{-1} shift^{17,18} observed in the spectrum of the uranium peroxide compound.

A summary of the analytical results (and the mole ratio values calculated from these results) for the reaction of either uranium peroxide hydrate starting compound with alcoholic KOH solutions is given in Table I.

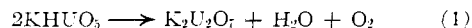
TABLE I

KOH, <i>M</i>	REACTION OF $H_2UO_5 \cdot H_2O$ WITH KOH					Mole ratio			
	U	Chemical analyses, K	% O-O	% H ₂ O	U	K	O-O	H ₂ O	
0.02	67.60	2.50	9.19	10.7	1.00	0.23	1.01	2.1	
.10	61.51	11.07	7.90	10.3	1.00	1.00	0.96	2.2	
.50	58.90	13.66	7.66	11.1	1.00	1.41	.97	2.5	
2.0	57.15	15.34	7.50	12.7	1.00	1.63	.98	2.9	
4.0	52.56	18.07	6.96	11.8	1.00	2.10	.99	3.0	

X-Ray diffraction patterns of the starting peroxide compound and of the potassium salts formed were used to supplement chemical analysis by ascertaining the existence of a homogeneous product. The product of reaction with 0.02 *M* KOH was, by this means, identified as a mixture of $H_2UO_5 \cdot H_2O$ and hydrated $KHUO_5$. Similarly, the products of reaction with 0.5 and 2.0 *M* KOH were identified as a mixture of hydrated $KHUO_5$ and K_2UO_5 .

The large excess of base required for the formation of the hydrated monobasic ($KHUO_5 \cdot 2H_2O$) and dibasic ($K_2UO_5 \cdot 3H_2O$) salts in alcoholic potassium hydroxide solutions can be explained by the ready hydrolysis of these salts to $H_2UO_5 \cdot H_2O$ in the presence of water. This hydrolytic tendency explains the failure of previous investigators to establish the acidic nature of the uranium peroxide compound *via* a simple acid-base reaction in aqueous media.^{19,20} Hydrated potassium peroxyuranates have been prepared, however, by other methods not designed to establish the acidic character of $H_2UO_5 \cdot H_2O$.

Formation of the hydrated monobasic salt, $KHUO_5 \cdot 2H_2O$, and the hydrated dibasic salt, $K_2UO_5 \cdot 3H_2O$, was verified by chemical analysis, X-ray diffraction techniques and a study of the thermal decomposition reactions of these salts. The monobasic salt was shown to decompose to potassium pyrouranate on heating in accordance with the equation



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(18) Ref. 17, pp. 257, 259, 296.

(19) H. Remy, "Treatise on Inorganic Chemistry," Vol. II, Trans. by J. S. Anderson, Elsevier Publishing Co., New York, N. Y., 1956, p. 201.

(20) N. V. Sidgwick, "The Chemical Elements and Their Compounds," Vol. II, Clarendon Press, Oxford, 1950, p. 1074.

(9) G. W. Watt, S. L. Achorn and J. L. Marley, *THIS JOURNAL*, **72**, 3341 (1950).

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(11) J. Mitchell, Jr., and D. M. Smith, "Aquametry," Interscience Publishers, Inc., New York, N. Y., 1948, pp. 65-102.

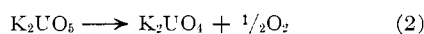
(12) M. M. Stimson and M. J. O'Donnell, *THIS JOURNAL*, **74**, 1805 (1952).

(13) U. Schiedt and H. Reinwein, *Z. Naturforsch.*, **7b**, 270 (1952).

(14) G. K. T. Conn and C. K. Wu, *Trans. Faraday Soc.*, **34**, 1483 (1938).

(15) G. Tridot, *Ann. Chim. (Paris)*, **10**, 225 (1955).

The dibasic salt similarly was shown to decompose to potassium uranate on heating in accordance with the equation



The formation of potassium pyrouanate and potassium uranate as thermal decomposition products was substantiated by X-ray diffraction patterns and chemical analyses.

Conclusions

The chemical reactions of the compound prepared by either the precipitation of uranium from uranyl nitrate solutions with hydrogen peroxide or the reaction of uranium trioxide with aqueous hydrogen peroxide can be suitably explained by the existence of a peroxyuranic acid structure. Of the two previously proposed acid structures (H_4UO_6 or $\text{H}_2\text{UO}_5 \cdot \text{H}_2\text{O}$), infrared spectral data, by establishing the presence of a hydrate water group, indicate that hydrated peroxyuranic acid ($\text{H}_2\text{UO}_5 \cdot \text{H}_2\text{O}$) most truly represents the chemical nature of the compound.

The uranium-oxygen-peroxyoxygen acid system shows a similarity to the known inorganic oxygen-peroxyoxygen acid systems. This similarity is

based on the preparation of the oxygen acid and the peroxyoxygen acid from the acid anhydride by the addition of water and peroxide, respectively. A comparison of the sulfur and uranium acid systems suitably illustrates this similarity.

SO_3	Acid anhydride	UO_3
H_2SO_3	Primary oxygen acid	H_2UO_4
H_2SO_5	Peroxyoxygen acid	H_2UO_5
$\text{H}_2\text{SO}_4 \cdot \text{H}_2\text{O}$	Hydrated oxygen acid	$\text{H}_2\text{UO}_4 \cdot \text{H}_2\text{O}$
$\text{H}_2\text{SO}_5 \cdot \text{H}_2\text{O}$	Hydrated peroxyoxygen acid	$\text{H}_2\text{UO}_5 \cdot \text{H}_2\text{O}$
$\text{H}_2\text{S}_2\text{O}_7$	Pyro (oxygen) acid	$\text{H}_2\text{U}_2\text{O}_7$

The preceding data and discussion were primarily intended to establish the structure of hydrated uranium peroxide through reaction with strong bases. In light of the previously established amphoteric character of other hexavalent uranium oxide hydrates, peroxyuranic acid would be expected to react, as a base, with strong acids.

Acknowledgment.—We wish to express our appreciation to F. H. Ford for obtaining and interpreting the X-ray diffraction patterns, to B. Gessiness and his staff for the analytical results, and to P. S. Gentile, L. H. Talley and D. A. Stock for their help in obtaining the above data.

CINCINNATI, OHIO

[CONTRIBUTION FROM THE LOW TEMPERATURE LABORATORY, DEPARTMENTS OF CHEMISTRY AND CHEMICAL ENGINEERING UNIVERSITY OF CALIFORNIA, BERKELEY]

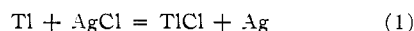
The Low Temperature Heat Capacity and Entropy of Thallous Chloride¹

By I. R. BARTKY AND W. F. GIAUQUE

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The heat capacity of thallous chloride has been measured from 15 to 310°K. The entropy at 298.15°K. was found to be 26.59 cal. deg.⁻¹ mole⁻¹. The heat capacity, entropy, $(F^0 - H_0^0)/T$ and $(H^0 - H_0^0)/T$ functions for TlCl are tabulated from 15 to 300°K. The entropy change calculated from the third law of thermodynamics for the cell reaction $\text{Tl} + \text{AgCl} = \text{TlCl} + \text{Ag}$ was found to be in good agreement with the cell temperature coefficients of Gerke provided the entropy change for the step $\text{Tl}(s) = \text{Tl}(\text{amalg})$ is calculated from $\Delta S = (\Delta H_{\text{calorimetric}} + FE)/T$ rather than from dE/dT . It is evidently difficult to obtain reliable cell temperature coefficients involving a metal electrode even when it is as soft as thallium. Third law results have been used to calculate these heats of reaction at 298.15°K.: $\text{Tl}(\text{cryst.}) + \text{AgCl} = \text{TlCl} + \text{Ag}$, $\Delta H^0 = -18,430$ cal. mole⁻¹; $\text{Tl} + \frac{1}{2}\text{Cl}_2 = \text{TlCl}$, $\Delta H^0 = -48,800$ cal. mole⁻¹.

Gerke² studied a number of cells in order to test the validity of the third law of thermodynamics by comparing the entropy changes as calculated from the temperature coefficients of the cell voltages with those calculated from the available low temperature heat capacity data by means of the third law. He found a discrepancy of 2.0 cal. deg.⁻¹ mole⁻¹ in the cell



The heat capacity data available at that early date often were inaccurate since the techniques of low temperature calorimetry were in the first stages of their development. Thus Gerke considered that the discrepancy had its origin in the heat capacity data and particularly in that on thallous chloride. The present work provides accurate heat capacity data for thallous chloride.

Calorimetry and Material.—The low temperature heat capacity was measured in an apparatus similar to that described by Giauque and Egan.³ The particular calorim-

eter was described by Kemp and Giauque⁴ and its most recent modification by Papadopoulos and Giauque.⁵ Briefly, the present calorimeter was of copper and the temperature was measured by a gold resistance thermometer-heater, for high precision, and Laboratory Standard Copper-Constantan Thermocouple No. 105 for simultaneous reference before and after every heat input. The thermocouple was compared with the triple (13.94°K.) and boiling points (20.36°K.) of hydrogen and the triple (63.15°K.) and boiling points (77.34°K.) of nitrogen, during the course of the present work.

0° was taken as 273.15°K. and 1 defined calorie was taken equal to 4.1840 absolute joules.

The thallous chloride was supplied 99.9+ % pure by the Chemical Commerce Co. It was received in the form of a rather voluminous precipitated powder. This material was heated to the melting point (about 430°), in a Pyrex beaker so that a large reduction in volume occurred. This eliminated the possibility that particles with microscopic properties could remain in the sample used for the heat capacity measurements as could be the case with a fine powder. The well-crystallized solid was broken easily with a mortar and pestle and the crystals were passed through an 8 mesh in. ⁻¹ screen so that they would pack well within the calorimeter. The use of this material, rather than the powder, at least doubled the amount of material which could be placed in the calorimeter and also improved the heat con-

(1) This work was supported in part by the National Science Foundation. The U. S. Government may reproduce this article.

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(5) M. N. Papadopoulos and W. F. Giauque, *ibid.*, **77**, 2710 (1955).