

LETTERS TO THE EDITOR

THERMODYNAMIC PROPERTIES OF SOME CHROMYL HALIDES

ONCE the spectroscopic measured frequencies and the moments of inertia of a polyatomic molecule are known it is possible to obtain the thermodynamical properties of the molecule. These properties have great practical importance since it is difficult and, sometimes, even impossible to measure these quantities experimentally. In certain cases the calculated values are more accurate than the experimental values. The reliability of the values of the force fields of vibrating molecules may be tested using the thermodynamical properties of the molecule.

TABLE I

Thermodynamic properties for CrO_2Cl_2 and CrO_2F_2

T (°K)	$C_p^{\circ*}$	$S^{\circ*}$	$\frac{H^{\circ} - E^{\circ*}}{T}$	$\frac{F^{\circ} - E^{\circ*}}{T}$
CrO_2Cl_2				
500	22.9680	91.2118	17.3919	73.8199
600	23.6893	95.4675	18.3854	77.0822
700	24.1806	99.1584	19.1803	79.9781
800	24.5262	102.4112	19.8281	82.5830
900	24.7765	105.3151	20.3648	84.9504
1000	24.9630	107.9357	20.8157	87.1200
1100	25.1050	110.3220	21.1995	89.1224
1200	25.2154	112.5113	21.5297	90.9815
1300	25.3029	114.5331	21.8167	92.7164
1400	25.3732	116.4109	22.0683	94.3426
1500	25.4306	118.1635	22.2906	95.8729
CrO_2F_2				
300	18.5420	75.2460	13.1083	62.1378
400	20.6394	80.8871	14.7459	66.1412
500	22.0444	85.6541	16.0746	69.5795
600	22.9875	89.7622	17.1532	72.6090
700	23.6351	93.3573	18.0357	75.3216
800	24.0925	96.5449	18.7658	77.7791
900	24.4248	99.4928	19.3771	80.0257
1000	24.6725	101.9306	19.8948	82.0948
1100	24.8515	104.3501	20.3381	84.0123
1200	25.0036	106.5202	20.7214	85.7988
1300	25.1251	108.5267	21.0559	87.4709
1400	25.2189	110.3923	21.3500	89.0423
1500	25.2954	112.1349	21.6106	90.5243

* Cal deg⁻¹ mole⁻¹.

From the vibrational assignments¹⁻³ of the chromyl halides CrO_2X_2 (X = Cl or F) under consideration, it is found that they belong to the C_{2v} point group with symmetry number as one. The thermodynamic quantities, viz., heat content, heat capacity, entropy and free energy, are calculated

on the basis of the ground electronic state with rigid rotator harmonic oscillator approximation⁵ and negligibly poor nuclear spin energy contribution. The results for the ideal gas state at atmospheric pressure are presented in Table I. From the structural parameters^{2,4} of the molecules, the principal moments of inertia are calculated and presented in Table II.

TABLE II
Principal moments of inertia

Molecule	I_{xx}^{**}	I_{yy}^{**}	I_{zz}^{**}
CrO_2Cl_2	330.83	158.67	271.84
CrO_2F_2	173.96	149.57	123.74

**a.m.u.Å².

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THIORIDAZINE HYDROCHLORIDE AS A NEW REAGENT FOR THE SPECTROPHOTOMETRIC DETERMINATION OF OSMIUM (VIII)

Introduction

DURING the spectrophotometric study of noble metals using thioridazine hydrochloride (TH)¹⁻³, it was found that TH formed blue-coloured oxidation product with osmium (VIII) in hydrochloric acid medium. This reaction is now utilised for the spectrophotometric determination of osmium (VIII).

Experimental

Stock solution of osmium (VIII) was prepared from osmium tetroxide in 0.2 M sodium hydroxide

and standardised as described by Ayres and Wells⁴. Working solutions were prepared as needed by the dilution of the stock solution. A 0.2% of aqueous solution of TH was used. All other solutions were prepared from reagent grade chemicals. Beckman Model DB spectrophotometer with matched 1 cm silica cells was used for absorbance measurements.

Procedure.—An aliquot of the sample solution containing 2.5–72 ppm of osmium was transferred to a 25 ml volumetric flask. 5 ml of 5 M hydrochloric acid and 5 ml of 0.2% TH solution were added and diluted to the mark with doubly distilled water. The solution was thoroughly mixed and the absorbance was measured after 10 minutes at 640 nm against a reagent blank prepared in the same way. The osmium concentration of the sample was calculated by reference to a previously prepared calibration curve.

Results and Discussion

Osmium (VIII) oxidises TH to a blue-coloured product which is thought to be a free radical³. The sensitivity and the stability of the blue-coloured product depend on the nature and strength of acid medium. The sensitivity of the reaction in four acid media (1.0 M) is in the order, HCl > H₂SO₄ > H₃PO₄ > HAC. The stability of the blue colour in 1.0 M HCl, H₂SO₄, H₃PO₄ and HAC is 25, 10, 5 and 4 minutes respectively. Hence hydrochloric acid medium is preferred. The maximum colour intensity is observed in 0.2–1.5 M HCl. Therefore 1.0 M hydrochloric acid is used in these studies.

The electronic spectrum of the blue-coloured species shows the maximum absorption around 640 nm with a shoulder at 490 nm. The reagent does not absorb at these wavelengths. A thirty-fold molar excess of TH over osmium is required for complete colour development. The constant absorbance values are obtained 5 minutes after adding the reagent to the osmium solution. The order of addition of reagents has no effect on the absorbance values which are insensitive to temperature in the range 5–40° C.

Beer's law is valid within the concentration range of 0.1 to 2.8 ppm of osmium and the optimum range is 1.0 to 2.4 ppm of osmium. At 640 nm, the molar absorptivity is 1.98×10^4 litre mole⁻¹ cm⁻¹. For log I₀/I = 0.001, the sensitivity of the reaction is 0.0096 µg Os cm⁻².

In order to assess the possible analytical applications of the reaction, the effect of diverse ions was studied. The following amounts (µg/ml) of foreign ions were found to give less than 2% error in the determination of 2 ppm of osmium;

Pt (IV) 15; Rh (III) 12; Ru (III) 1; Ir (III) 15; Co (II) 100; Ni (II) 150; UO₂ (II) 100; fluoride 1100; chloride 1800; bromide 800; nitrate 900; sulphate 1000; phosphate 300; oxalate 850; EDTA 10. Iodide, thiosulphate, Pd (II), Au (III), Fe (III), Ag (I), Ce (IV) and V (V) interfere seriously. Attempts to increase the tolerance limits of some cations were unsuccessful.

Determination of osmium in ores.—Synthetic mixtures containing platinum metals corresponding to osmiridium or syserkite were prepared and the osmium content was determined. The results are given in Table I.

TABLE I
Determination of osmium in synthetic mixtures corresponding to osmiridium or syserkite

Osmium present ppm	Rh, ppm	Ir, ppm	Ru, ppm	Pd ppm	Pt, ppm	Osmium found, ppm
1.00	..	0.250	0.150	..	0.050	1.02
1.50	..	0.425	0.225	..	0.075	1.56
2.00	..	0.500	0.300	..	0.100	2.05

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STUDIES IN THIADIAZOLES: SYNTHESIS OF SOME 2-SUBSTITUTED-5-MERCAPTO-1, 3, 4-THIADIAZOLES

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4-ARYLTHIOSEMICARBAZIDES (Ar NH-C-NHNH₂) on cyclisation yield 2-arylamino-5-mercapto-1, 3, 4-thiadiazoles which have been found to be biologically active¹. The SH group is an important toxophore as —OH especially to fungi² and when a heterocyclic compound contains an —SH group adjacent to a nitrogen atom, useful fungitoxic compounds are often obtained because of the possibility of chelation^{2,3}. The 2-arylamino-5-mercapto-1, 3, 4-thiadiazoles fulfil these requirements and therefore a study of these compounds was undertaken with a view to studying their fungicidal activity.

In the present communication six thiadiazoles have been prepared by the reaction of 4-arylthiosemicarbazides with carbon disulphide and diethylformamide⁴. (i) 4-Arylthiosemicarbazides were prepared