

controversy as to whether the isomers represent electromers according to the theory of Kharasch¹ or are merely *cis* and *trans* formations of 2-pentene.

As already pointed out, the total surface energies of the three isomers show appreciable differences. Part of this divergence may be attributed to experimental error, the lack of accurate vapor pressure data and impurity of compounds, but it is doubtful whether it would account for a gradual decrease of almost 5 ergs in the total surface energy. According to Traube the "*trans*" modification has usually the smallest density,¹⁰ which would indicate that the metastable form represented the "*cis*" compound.

Summary

1. The densities and surface tensions of the two 2-isomers of 2-pentene and 2-methyl-2-butene have been measured over a range of temperature of 150°.

2. The total surface energies of the three compounds differ considerably at different temperatures.

3. The observed parachor agrees tolerably well with the calculated value but shows a decrease with rise in temperature.

4. The Eötvös or Ramsay-Shields constant is higher than the normal.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF RUTGERS UNIVERSITY]

COPPER, COBALT, NICKEL, ZINC AND CADMIUM TETRAPYRIDINE FLUOSILICATES¹

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The salts of fluosilicic acid have come into extensive use, in recent years, as insecticides. As a result, a number of investigations of the properties of some of these salts have appeared. In a study of the solubility of certain of these salts, reference² was found in the literature to the effect that copper fluosilicate is insoluble in pyridine. When an experiment was performed to test the degree of solubility, it was found that whereas the compound does not dissolve appreciably, a reaction occurs which results in the formation of a new compound. Similar compounds were also formed with the fluosilicates of cobalt, nickel, zinc and cadmium. These new compounds are described in the present paper. Attempts to prepare

¹⁰ Traube, *Ann.*, **240**, 46 (1886).

¹ This paper is based on a thesis submitted by Walter T. L. Ten Broeck, Jr., to the Faculty of Rutgers University, in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

² J. W. Mellor, "Comprehensive Treatise on Inorganic and Theoretical Chemistry," Longmans, Green and Co., New York, 1925, Vol. VI, p. 950.

similar compounds containing quinoline or nicotine in place of pyridine were not successful.

Experimental Part

Materials Used.—Basic copper carbonate, and the normal carbonates of zinc, nickel, cadmium and cobalt, of the highest purity reagent grade obtainable, were used without further purification. Fluosilicic acid in water solution, containing approximately 30% by weight of the acid, was used. Its exact concentration was determined by titration. The pyridine also was of the highest purity obtainable.

Preparation of the Compounds.—The method of preparation of the compounds was the same in all cases. The carbonate of the metal was added in the cold to a solution of fluosilicic acid, the operation being carried out in a platinum dish. When effervescence ceased, the solution was filtered through paper to separate the excess of the carbonate, a few drops of hydrofluoric acid was added and the solution evaporated to small volume on the water-bath. The solution was then cooled and the crystals of the metal fluosilicate were collected on a filter.

The crystals of the metal fluosilicate were dissolved in water and pyridine was added slowly. There was a considerable evolution of heat and the solution was therefore cooled at intervals. Since the metal pyridine fluosilicates are much less soluble in water than the metal fluosilicates, the former compounds were obtained as precipitates in the form of fine crystals, when the pyridine was added to a moderately concentrated solution of the salt. The precipitates were filtered with suction, washed with a little pyridine, and were dried in an evacuated desiccator over calcium oxide or potassium hydroxide. These crystals were redissolved in water, and any small quantity of silica present was filtered off. The solution was then again evaporated, yielding a well crystallized product.

Analysis of the Compounds.—A complete analysis of the compounds involved a determination of the metals, silicon, fluorine, pyridine and water. A weighed portion of the salt was fumed with concentrated sulfuric acid. This procedure removed the silicon tetrafluoride and changed the pyridine to pyridine sulfate, while the metals remained as soluble sulfates. After dilution the metals were determined electrolytically by the usual methods.

A separate portion was weighed out for the determination of silicon. In the case of the copper salt the copper was removed by electrolyzing the solution rendered weakly acid with nitric acid. Zinc and cadmium were removed by deposition from solutions weakly acid with acetic acid containing some sodium acetate. In the case of the nickel and cobalt compounds, a half-gram sample was dissolved in 100 cc. of water and 10 g. of ammonium chloride was added to the solution. Forty cubic centimeters of ammonium hydroxide was added, and the silica was filtered and washed. The silica was examined for cobalt and nickel oxide and found to be free from them. The cobalt and nickel were then determined in the filtrates. For the determination of silicon, one-half gram of the compound was dissolved in 100 cc. of water, 10 g. of ammonium chloride was added, and then 40 cc. of concentrated ammonium hydroxide. The solution was allowed to stand for twenty-four hours and the precipitated silica was collected on a filter and dried. The ammoniacal solution was electrolyzed under the proper conditions to remove the metal. The solution still contained some silica, and this was removed by the method recommended by Treadwell-Hall³ for determining silica in fluosilicates.

³ Treadwell-Hall, "Analytical Chemistry," 4th ed., John Wiley and Sons, Inc., New York, 1915, Vol. II, p. 484.

Fluorine was determined in the filtrate from the silicic acid precipitation. Ammonium salts were removed by repeated treatment with sodium carbonate and boiling, after which the solution was concentrated to approximately 100 cc. An excess of 3 *N* calcium chloride was added, and the combined precipitate of calcium carbonate and calcium fluoride was washed with hot water, dried and ignited. The calcium oxide was dissolved with acetic acid and the insoluble calcium fluoride was collected on a filter, washed, dried, ignited and weighed. It is well recognized that this method of analysis gives low results for fluorine. Pyridine was determined by adding an excess of potassium hydroxide solution to a weighed quantity of the compound, and distilling the pyridine into a standard solution of sulfuric acid. The excess sulfuric acid was determined by titration with standard alkali, using methyl orange as indicator. In this case the acid was standardized by titration against known quantities of pyridine.

The copper compound contained water, and it was therefore necessary to determine this constituent also. The method used was that of Jannasch.³ A weighed quantity of the compound was mixed with dried lead oxide in a combustion boat, and the boat introduced into a tube provided with a plug of lead oxide. The tube was connected with a U-tube containing sulfuric acid and pumice. Dry nitrogen was passed through the tube while it was heated gradually to 150°. The quantity of water and pyridine absorbed in the sulfuric acid was determined by weighing. By subtracting the weight of pyridine from the total weight, the quantity of water was obtained.

The density of the crystals was determined in a specific gravity bottle, at 25°, using xylene as the confining liquid.

The refractive index of the crystals⁴ was determined by placing them on a slide, immersing in drops of oil of known index of refraction, and observing the relative indices of oil and crystals by means of the Becke line.

Description of the Compounds.—Table I contains the composition of the compounds determined by analysis, and the composition calculated from the formulas. It also contains a statement of the color, density, crystal system and refractive index of these compounds.

Thermal Decomposition.—When the metal pyridine fluosilicates which have been described are heated, an evolution of pyridine is first observed. At higher temperatures silicon tetrafluoride is also given off. In order to gain some insight into the relative stability of these compounds, the method used by Biltz⁵ in his studies of ammonia compounds was employed. A definite weight of the salt is placed in an evacuated apparatus, heated to a definite temperature, and the pressure of the volatile substance is meas-

⁴ We are indebted to Professor A. C. Hawkins of the Geology Department for assistance in the determination of the optical properties.

⁵ W. Biltz and W. Hansen, *Z. anorg. allgem. Chem.*, 127, 1–33 (1923).

ured. The volatile product is then pumped off repeatedly until there is a drop in the equilibrium pressure. At this point the temperature is raised until the pressure returns to the original value, when the process is continued at the higher temperature.

When this method is applied to the cadmium, zinc, copper and nickel tetrapyrindine fluosilicates, very low dissociation pressures with pyridine as the volatile product are observed. When the temperature is raised sufficiently to obtain a workable pressure, there is also an evolution of silicon tetrafluoride. Only in the case of the cobalt compound was it possible to obtain significant data. Figure 1 represents graphically the relation between composition and temperature at pressures of 6, 11 and 16 mm. of mercury.

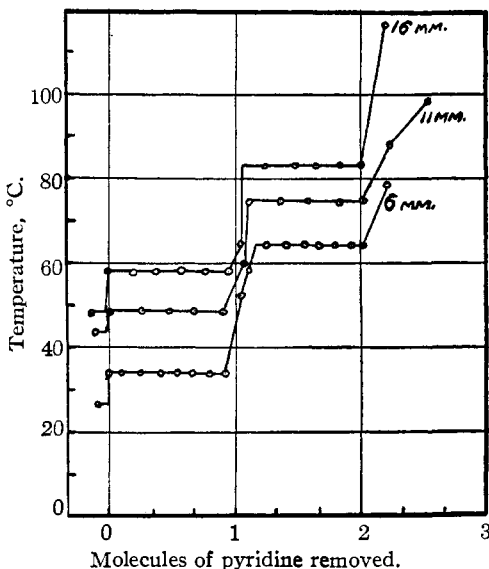
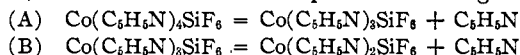


Fig. 1.

temperature at pressures of 6, 11 and 16 mm. of mercury. In the case of the cobalt compound, the dissociation takes place according to the reactions



The dissociation pressures corresponding to these reactions are

Pressure, mm.	6	11	16
Reaction A, °C.	34.9	48.3	58.1
Reaction B, °C.	64.3	75.2	83.1

TABLE I
DATA ON THE COMPOUNDS

	Cupric tetrapyrindine fluosilicate monohydrate, $\text{Cu}(\text{C}_5\text{H}_5\text{N})_4\text{SiF}_6 \cdot \text{H}_2\text{O}$		Cadmium tetrapyrindine fluosilicate, $\text{Cd}(\text{C}_5\text{H}_5\text{N})_4\text{SiF}_6$		Zinc tetrapyrindine fluosilicate, $\text{Zn}(\text{C}_5\text{H}_5\text{N})_4\text{SiF}_6$		Nickel tetrapyrindine fluosilicate, $\text{Ni}(\text{C}_5\text{H}_5\text{N})_4\text{SiF}_6$		Cobalt tetrapyrindine fluosilicate, $\text{Co}(\text{C}_5\text{H}_5\text{N})_4\text{SiF}_6$	
	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.
Copper, %	11.77	11.77								
Cadmium, %			19.70	19.70						
Zinc, %					12.49	12.48				
Nickel, %							11.31	11.35		
Cobalt, %									11.39	11.40
Pyridine, %	58.81	58.61	55.19	55.41	60.97	60.39	61.24	61.17	61.09	61.16
Silicon, %	5.22	5.20	4.98	4.92	5.42	5.36	5.39	5.43	5.45	5.43
Fluorine, %	20.14	21.11	19.17	19.97	21.00	21.77	21.37	22.05	21.52	22.04
Water, %	3.13	3.33								
Color	Dark purplish-blue		White		White		Pale bluish-green		Pink	
Density, 25°	2.108		2.282		2.197		2.307		2.215	
Crystal system	Orthorhombic		Triclinic		Orthorhombic		Orthorhombic		Orthorhombic	
Refractive index	1.72 ± 0.005		1.545 ± 0.002		1.540 ± 0.002		1.571 ± 0.002		1.601 ± 0.002	

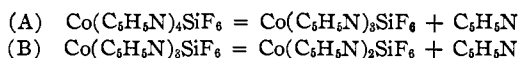
The thermal dissociation of cadmium tetrapyrindine fluosilicate gave a pressure of approximately 4 mm. at 77°, but there was also a slow evolution of silicon tetrafluoride with the formation of a sublimation product of pyridine and silicon tetrafluoride. This system, therefore, was not investigated further. In the cases of copper, nickel and zinc, the dissociation pressures were even lower than with the cadmium compound.

Summary

Five new complex salts of fluosilicic acid have been prepared from solution and have been described. These are

Cupric tetrapyrindine fluosilicate monohydrate	$\text{Cu}(\text{C}_5\text{H}_5\text{N})_4\text{SiF}_6 \cdot \text{H}_2\text{O}$
Cobalt tetrapyrindine fluosilicate	$\text{Co}(\text{C}_5\text{H}_5\text{N})_4\text{SiF}_6$
Nickel tetrapyrindine fluosilicate	$\text{Ni}(\text{C}_5\text{H}_5\text{N})_4\text{SiF}_6$
Zinc tetrapyrindine fluosilicate	$\text{Zn}(\text{C}_5\text{H}_5\text{N})_4\text{SiF}_6$
Cadmium tetrapyrindine fluosilicate	$\text{Cd}(\text{C}_5\text{H}_5\text{N})_4\text{SiF}_6$

When the cobalt tetrapyrindine fluosilicate is heated it loses pyridine, as represented by the reactions



The dissociation pressures of these two reactions have been measured up to a temperature of 83°.

At higher temperatures silicon tetrafluoride is also given off.

The copper, nickel, zinc and cadmium salts do not give appreciable pyridine pressures until a temperature is reached at which silicon tetrafluoride is also evolved.

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ALUMINO-OXALATES

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The preparation of salts of alumino-oxalic acid has been described in detail by Rosenheim¹ who obtained derivatives of various types such as $3\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{C}_2\text{O}_3 \cdot 9.5\text{H}_2\text{O}$; $2\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 5\text{C}_2\text{O}_3 \cdot 8\text{H}_2\text{O}$, $2\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 4\text{C}_2\text{O}_3 \cdot 6\text{H}_2\text{O}$ and $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 4\text{C}_2\text{O}_3 \cdot 10.5\text{H}_2\text{O}$. The present work was undertaken primarily with the intention of studying the mode of dissociation of the various types, other than the first, which is the normal sodium alumino-oxalate already discussed by Burrows and Walker.²

Unfortunately we have not succeeded in isolating any of these other types according to the method described by Rosenheim, using freshly

¹ Rosenheim, *Z. anorg. Chem.*, **11**, 175 (1896).

² The water content of this salt has already been discussed by one of us (Burrows and Walker, *J. Chem. Soc.*, **123**, 2738 (1923)).