

sometimes observed when the temperature of the gas was as low as  $-70^{\circ}$ .

It was also noticed that cold surfaces in the snow trap usually became encrusted with a thin layer of adhering crystals.

The target was then replaced with a 15 cm. length of 2.5 cm. diameter copper tubing jacketed to maintain any desired temperature. This tube was connected to one pole of a 9000-volt transformer and the other pole was attached to a needle extending about 2 cm. down the center of the tube. When the fog was started and the current turned on, a deposit of snow rapidly formed inside the tube and on the needle. When this snow was scraped away there was always a strongly adhering deposit on the metal walls which we took to be signs of the existence of liquid droplets in the vapor stream. Precautions were taken to prove that this deposit did not come from infiltration of air from the outside, from water vapor carried along in the gas stream or from the adhesion of snow. The lowest gas stream temperature obtained was  $-72^{\circ}$ .

It was our original intention to carry these observations down to liquid air temperatures. Crystallization and adhesion seemed possible at the lowest temperatures obtainable with solid carbon dioxide so that it can safely be concluded

that at  $-72^{\circ}$  water is not yet cold enough to be vitreous and stable.

Since the completion of the above experiments, however, Burton and Oliver<sup>25</sup> have published unequivocal x-ray evidence that water sublimed onto a copper surface at  $-155^{\circ}$  forms an amorphous deposit that remains stable up to about  $-110^{\circ}$ , where it crystallizes.

It is pleasant to record here my indebtedness to my former students, Wm. E. Lieb, J. E. Drummond and I. R. Freeman, for the long hours that they spent in the laboratory laying the experimental foundation for this paper.

### Summary

It is demonstrated that water in isolated droplets can readily undercool and remain without freezing at temperatures customarily used in the measurement of "bound" water by the freezing method. It is pointed out that in colloids, and particularly in biologic tissues, the conditions are favorable for the isolation of small masses of water during freezing which then may, and probably often do, remain liquid, contributing substantially to the quantity of so-called "bound" water.

(25) E. F. Burton and W. F. Oliver, *Nature*, **135**, 505 (1935).

RECEIVED APRIL 10, 1936

---

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF COLORADO]

## Some Double Salts of Indium and Organic Bases

BY JOHN B. EKELEY AND HERBERT A. POTRATZ

Various double salts of indium and organic bases have been prepared, their formulas determined and their optical properties<sup>1</sup> studied when possible.

Indium halides form double salts as herein described with substituted ammonium halides in the molecular ratios 1:1, 1:2, 1:3 and 1:4, crystallizing without water of crystallization. Hitherto only one example with a ratio of 1:4 has been observed, namely, indium quinoline hydrochloride.

(1) Measurements were made by M. E. Hultquist. The refractive indices were determined by the immersion method using the Becke line as a criterion of match. Interference figures were used as a means of determining optical orientation of the crystals. The temperature at which the indices were taken was  $25 \pm 1^{\circ}$ , and the source of light was ordinary daylight from a window of northern exposure.

Similarly indium sulfate and substituted ammonium sulfates form double salts, so far as studied, in the molecular ratios 1:1 and 1:3, crystallizing with water of crystallization, which except in the amylammonium salt was held so tenaciously that it was not expelled entirely after heating for many hours at  $140-170^{\circ}$ . Attempts to form alums analogous to the known indium ammonium alum failed.

Indium halides and the corresponding trialkyl sulfonium halides form double salts, the indium trimethyl sulfonium chloride crystallizing with water of crystallization in the molecular ratios 2:4:3, while the corresponding trimethyl and triethyl iodides crystallize in the anhydrous form in the ratios 1:1.

### Experimental Data

#### Indium Substituted Ammonium Halides.—

The double indium substituted ammonium halides were prepared by mixing concentrated methanol or ethanol solutions of the constituent salts from which crystals were either obtained at once or upon evaporation of the mixture. Recrystallization from alcohol solution similar to the one used in preparation of the salt yielded the pure compound: very soluble in water, sparingly in cold, readily in the hot alcohols, insoluble in ether or chloroform. Analyses were made on the salts dried at 110°.

#### Indium Substituted Ammonium Sulfates.—

The indium substituted ammonium sulfates were prepared by evaporating at room temperature mixed saturated water solutions of the constituents. The crystals thus obtained were recrystallized,

washed with 95% ethanol and dried at room temperature. These salts do not melt below 300°.

**Indium Alkyl Sulfonium Halides.**—On mixing saturated aqueous methanol solutions of indium chloride and trimethylsulfonium chloride, crystals separated at once. Recrystallized from methanol they lose water of crystallization over phosphorus pentoxide. They are very soluble in water, in hot or cold ethanol, or in hot methanol; quite soluble in cold methanol, insoluble in ether or chloroform. Heated to 110° the crystals decompose. Rapid heating in a capillary tube gives a m. p. of 203–204° (uncorr.) with decomposition.

Similarly, saturated aqueous solutions of indium iodide and trimethyl or triethyl sulfonium iodide yield precipitates. The double iodides were obtained anhydrous by recrystallization of the dry precipitates from absolute methanol; m. p. 149–

TABLE I  
INDIUM SUBSTITUTED AMMONIUM HALIDES

Formula	M. p., °C.	Indium, %		Chlorine or bromine, %	
		Calcd.	Found	Calcd.	Found
4CH <sub>3</sub> NH <sub>3</sub> Cl·InCl <sub>3</sub>	Above 300	23.36	23.49 23.66	50.53	50.52 50.88
4(CH <sub>3</sub> ) <sub>2</sub> NH <sub>2</sub> Cl·InCl <sub>3</sub>	215–217	20.98	21.10 20.84	45.37	45.44 45.49
3(CH <sub>3</sub> ) <sub>3</sub> NHCl·InCl <sub>3</sub>	196–198	22.60	22.91 22.46	41.90	41.99 41.94
2(CH <sub>3</sub> ) <sub>4</sub> NCl·InCl <sub>3</sub>	Above 300	26.06	26.02 26.13	40.27	40.03 40.07
2(CH <sub>3</sub> ) <sub>4</sub> NBr·InBr <sub>3</sub>	236–238	17.32	17.53 17.00	60.31	60.33 60.03
2(C <sub>2</sub> H <sub>5</sub> ) <sub>4</sub> NCl·InCl <sub>3</sub>	275–277	20.78	20.88 20.50	32.10	32.38 31.99
(C <sub>2</sub> H <sub>5</sub> ) <sub>4</sub> NBr·InBr <sub>3</sub>	289–291	20.33	20.68 20.14	56.62	56.46 56.72

#### OPTICAL PROPERTIES

Salt	Form	System	Opt. sign	Elongation	Indices of refraction				
					α	β	γ	ω	ε
4CH <sub>3</sub> NH <sub>3</sub> Cl·InCl <sub>3</sub>	Short prisms	Tetragonal	+	—				1.582	1.595
4(CH <sub>3</sub> ) <sub>2</sub> NH <sub>2</sub> Cl·InCl <sub>3</sub>	Plates	Orthorhombic	+	≠	1.550	1.560	1.574		
3(CH <sub>3</sub> ) <sub>3</sub> NHCl·InCl <sub>3</sub>	Flat prisms	Tetragonal	+	+				1.546	1.549
2(CH <sub>3</sub> ) <sub>4</sub> NCl·InCl <sub>3</sub>	Twinned prisms and plates	Monoclinic	—	Not detd.	1.54+	1.550	1.555		
2(C <sub>2</sub> H <sub>5</sub> ) <sub>4</sub> NCl·InCl <sub>3</sub>	Basal plates	Tetragonal	—	+				1.583	1.565
2(C <sub>2</sub> H <sub>5</sub> ) <sub>4</sub> NBr·InBr <sub>3</sub>	Pseudo-prisms	Isometric			1.599				
(C <sub>2</sub> H <sub>5</sub> ) <sub>4</sub> NBr·InBr <sub>3</sub>	Hexagonal prisms	Hexagonal	+	+				1.609	1.614

TABLE II  
INDIUM SUBSTITUTED AMMONIUM SULFATES

Formula	Calcd.	Indium, %		Calcd.	Sulfate	
		Found	Found		Calcd.	Found
(CH <sub>3</sub> NH <sub>3</sub> ) <sub>2</sub> SO <sub>4</sub> ·In <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> ·4H <sub>2</sub> O	30.62	30.61	30.72	51.23	51.09	50.73
2(C <sub>2</sub> H <sub>5</sub> NH <sub>2</sub> ) <sub>2</sub> SO <sub>4</sub> ·2In <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> ·7H <sub>2</sub> O	29.86	30.14	30.11	49.97	49.78	49.75
2((C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> NH <sub>2</sub> ) <sub>2</sub> SO <sub>4</sub> ·2In <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> ·7H <sub>2</sub> O	27.83	27.84	27.95	46.57	46.43	...
2((C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> NH <sub>2</sub> ) <sub>2</sub> SO <sub>4</sub> ·2In <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> ·5H <sub>2</sub> O	28.45	28.63	28.51	47.62	47.51	...
3( <i>n</i> -C <sub>8</sub> H <sub>17</sub> NH <sub>2</sub> ) <sub>2</sub> SO <sub>4</sub> ·In <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> ·2H <sub>2</sub> O	16.75	16.77	16.88	42.06	42.32	42.65
(C <sub>8</sub> H <sub>5</sub> CH <sub>2</sub> NH <sub>2</sub> ) <sub>2</sub> SO <sub>4</sub> ·In <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> ·6H <sub>2</sub> O	24.47	24.69	24.47	40.96	41.29	40.84

#### OPTICAL PROPERTIES

Salt	Form	System	Opt. sign	Elongation	Refractive indices		
					α	β	γ
2(C <sub>2</sub> H <sub>5</sub> NH <sub>2</sub> ) <sub>2</sub> SO <sub>4</sub> ·2In <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> ·7H <sub>2</sub> O	Prisms	Monoclinic	+	≠	1.537	1.552	1.575
(C <sub>8</sub> H <sub>5</sub> CH <sub>2</sub> NH <sub>2</sub> ) <sub>2</sub> SO <sub>4</sub> ·In <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> ·6H <sub>2</sub> O	Multiple twinned prisms	Monoclinic	—	+	<sup>a</sup>	1.552	1.580

<sup>a</sup> The other double salts of this series yielded such extremely minute crystals that the optical properties could not be determined, nor could the alpha index be determined in the case of the benzyl ammonium salt.

TABLE III  
 INDIUM TRIALKYL SULFONIUM HALIDES

Formula	Indium, %		Chlorine or iodine, %			Water	
	Calcd.	Found	Calcd.	Found	Calcd.	Found	
$4(\text{CH}_3)_3\text{SCI}\cdot 2\text{InCl}_3\cdot 3\text{H}_2\text{O}$	24.25	24.20 24.27	37.45	37.63 37.19	5.71	5.88	
$(\text{CH}_3)_3\text{SI}\cdot \text{InI}_3$	16.40	16.64 16.68	72.57	72.31 72.08			
$(\text{C}_2\text{H}_5)_3\text{SI}\cdot \text{InI}_3$	15.47	15.75 15.63	68.46	68.37 68.63			

150° and 145–147°, respectively. In ether these iodides decompose slowly with the liberation of iodine.

**Optical Properties.**—Indium trimethylsulfonium chloride crystallized in such irregularly twinned monoclinic prisms that the refractive indices could not be determined. Indium trimethylsulfonium iodide yielded anisotropic crystals whose indices of refraction were greater than that of methylene iodide. Indium triethylsulfonium

iodide gave such extremely minute crystals that the optical properties could not be determined.

### Summary

Various double chlorides, bromides, iodides and sulfates of indium with the corresponding substituted ammonium and sulfonium salts have been prepared, their formulas determined, and when possible their optical properties.

BOULDER, COLORADO

RECEIVED JANUARY 27, 1936

[CONTRIBUTION FROM THE BIOCHEMICAL LABORATORY, UNIVERSITY OF NEBRASKA COLLEGE OF MEDICINE]

## The Oxidation of Amino Acids with Sodium Hypobromite

BY ALVIN H. FRIEDMAN AND SERGIUS MORGULIS

### Introduction

The problem of the oxidation of the amino acids in the body is one still awaiting a satisfactory solution. The mechanism of the oxidation is not accessible to direct experimentation. The close relationship among the amino acids, ketonic acids and hydroxy acids furnishes a basis for the interpretation of the mode of utilization of amino acids by the body. Experiments on perfusing the liver of various animals with different amino acids have demonstrated the presence of ketonic acids in the perfusate. The deamination of the amino acids in the liver is also well established. Amino acids may also be decarboxylated in the organism, as is shown by the presence in the body fluids of histamine and tyramine.

The oxidation of the amino acids *in vitro* has been the subject of many investigations, both from a purely chemical standpoint and from the point of view of its bearing on the mechanism of the amino acid metabolism in the organism. Amino acids are resistant to hydrolyzing agents, and they do not react readily with reducing agents, but are very reactive with oxidizing agents in general.<sup>1,2,3,4</sup>

The production of aldehydes from the amino acids has been demonstrated by many authors with a diversity of oxidizing agents.<sup>5,6,7</sup> Langheld<sup>8</sup> was the first to study the effect of sodium hypochlorite on the amino acids and found that carbon dioxide, ammonia, and "C-armere Aldehyde" are produced in the reaction. Dakin's<sup>9</sup> work on the reaction of amino acids with sodium hypochlorite followed Langheld's. Dakin used sodium-*p*-toluene sulfonchloramide (chloramine-T) and found that although this reagent contained no free sodium hypochlorite, it acted in the same manner as would a solution of sodium hypochlorite, chlorination of the amino group to give an N-chloro amino acid being the first product which decomposes yielding ammonia, carbon dioxide and the corresponding aldehyde.

The reaction of the amino acids with sodium hypobromite has not been very extensively studied. Jolles<sup>10</sup> long ago noticed that when glycine is acted upon by sodium hypobromite a compound is formed which is precipitable with phosphotungstic acid. This compound, as can

- (1) W. Heintz, *Ann. Chem. Pharm.*, **145**, 214 (1868).
- (2) R. M. Herbst and H. T. Clarke, *J. Biol. Chem.*, **104**, 769 (1934).
- (3) K. Kraut and F. Hartmann, *Ann. Chem. Pharm.*, **133**, 101 (1865).
- (4) A. Strecker, *ibid.*, **75**, 37 (1850).

- (5) Sh. Akrabi, *Proc. Imp. Acad. Japan*, **3**, 672 (1927).
- (6) E. S. Hill, *J. Biol. Chem.*, **95**, 197 (1932).
- (7) O. Warburg, *Science*, **61**, 577 (1925).
- (8) K. Langheld, *Ber.*, **42**, 392 (1909).
- (9) H. D. Dakin, *Biochem. J.*, **10**, 319 (1916); **11**, 79 (1917).
- (10) H. Jolles, *Z. physiol. Chem.*, **31**, 391 (1900).