(This result may also be derived from the Clausius–Clapeyron formula considering the melt as a regular solution.) The calculated curve checks only fairly with W. Eitel's measurements of the same phase diagram. However, there is also quite a difference in decomposition temperature for $CaCO_3$(s) at p_{CO_2} = 1 atm. given by W. Eitel (900°) and given by K. Kelley (884°). Our calculations are based upon K. Kelley's data.

The authors express their thanks to Det Videnskapelige Forskningsfond av 1919 and Norges tekniske høgskoles Fond for grants.

Summary

1. By means of a simple gravimetric procedure the composition of calcium carbonate–alkali carbonate melts in equilibrium with solid calcium oxide at a carbon dioxide pressure of 1 atm. has been determined.

2. On the basis of these results calculation of the activity coefficient of calcium carbonate in the melt is discussed. It follows that the carbonate mixtures behave as regular solutions.

3. The heat of fusion of calcium carbonate is calculated to 3400 cal.

TRONDHEIM, NORWAY RECEIVED AUGUST 4, 1948

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

Reactions of the Silver Salts of Carboxylic Acids with Iodine in the Presence of Some Tertiary Amines

BY RALPH A. ZINGARO, JUDSON E. GOODRICH, JACOB KLEINBERG AND CALVIN A. VANDERWERF

Recent reports[1,2] that monopyridine iodine (I) *p*-nitrobenzoate is toxic *in vitro* to certain fungi have reawakened interest in base stabilized iodine salts of organic acids.[3]

The purpose of the present work was the preparation of a series of positive iodine salts of organic acids, using pyridine or α- or β-picoline as the coördinating agents, with the intent of finding new compounds which may be effective against bacteria and fungi. Thirty-one of these salts have been prepared and pertinent data concerning them are collected in the tables. The percentage yields are based on the silver salt used and not on the amount of iodine which reacted. In those cases where pyridine was the coördinating agent, the aromatic acids used were selected in such a way as to permit comparisons of the effects on the yield of desired product of various substituents at different positions on the aromatic acid ring.

In many of the reactions where the yield of iodine salt was low, recovery of appreciable free acid was realized even under rigorously anhydrous conditions. For example, in the attempt to prepare α-picoline iodine (I) *p*-bromobenzoate, *p*-bromobenzoic acid was recovered in over 70% yield. This may mean that the formation of the iodine compound and the formation of the free acid are competing reactions.

TABLE I

DERIVATIVES OF α- AND β-PICOLINE IODINE (I)

	α				β			
	M. p., °C. (uncor.)	Yield, %	Iodine, %		M. p., °C.	Yield, %	Iodine, %	
			Calcd.	Found			Calcd.	Found
Benzoate	122–124dec.	9	37.2	37.1 36.9	123–126dec.	24	37.2	37.1 37.2
o-Nitrobenzoate	116–119dec.	14	32.9	32.7 32.6	88–91	36	32.9	33.0 33.0
m-Nitrobenzoate	139–143	53	32.9	33.0 32.8	134–137dec.	32	32.9	32.5 32.5
p-Nitrobenzoate	163–165dec.	14	32.9	32.9 32.9	188–191dec.	52	32.9	33.0 32.8
3,5-Dinitrobenzoate	159–162dec.	64	29.4	29.3 29.2	164–167dec.	32	29.4	29.1 29.1
p-Chlorobenzoate	113–116dec.	21	33.8	34.2 34.0	129–132dec.	17	33.8	33.6 33.5
p-Bromobenzoate	......	..	..	.. ..	127–129dec.	14	30.2	30.3 30.2
p-Iodobenzoate	118–121dec.	30	27.2	27.2 26.9	116–120dec.	50	27.2	27.0 27.5

Experimental

Preparation of Reagents.—Since positive iodine compounds decompose in the presence of water, anhydrous conditions must be maintained throughout in their preparation. The chloroform and Skellysolve A were dried over calcium chloride and distilled; the commercial absolute ether was dried over sodium and distilled. The pyridine and α- and β-picoline were dried over sodium hydroxide pellets for two weeks and distilled, the distillates boiling at 114.5 and 128.1° at 740 mm. and 141.7° at 735 mm., respectively, being collected.

Preparation of Silver Salts of the Acids.—The organic acid was dissolved in hot alcohol and a hot aqueous solu-

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(1) Kleinberg, Novak and Gerberg, *Proc. Soc. Exp. Biol. Med.*, **58**, 238 (1945).

(2) Kleinberg and Meyer, *Science*, **104**, 398 (1946).

(3) The following references describe the intermediate complex compounds formed by the action of iodine on the silver salts of organic acids, the various types of decomposition of these substances, mechanisms proposed for these reactions, and the use of pyridine as a coördinating base in the formation of positive iodine salts of organic acids: (a) Simonini, *Monatsh.*, **14**, 81 (1893); (b) Wieland and Fischer, *Ann.*, **446**, 49 (1925); (c) Hershberg, *Helv. Chim. Acta*, **17**, 351 (1934); (d) Prévost. *Compt. rend.*, **196**, 1129 (1933); (e) Birckenbach and Meisenheimer, *Ber.*, **69B**, 723 (1936); (f) Carlsohn, "Über eine neue Klasse von Verbindungen des positiv einwertigen Iods," Verlag von S. Hirzel, Leipzig, 1932.

TABLE II[a]

DERIVATIVES OF MONOPYRIDINE IODINE (I)

Salt	M. p., °C. (uncor.)	Yield, %	Per cent. Iodine as I^+ Calcd.	Found	
o-Nitrobenzoate	120–121	36	34.1	33.9	34.0
m-Nitrobenzoate	[b]	55	34.1	34.1	33.8
3,5-Dinitrobenzoate	157dec.	64	30.0	30.0	29.7
α-Naphthoate	109–112d.	48	33.6	33.5	33.5
p-Chlorobenzoate	105–109d.	47	35.1	35.3	35.1
2,4-Dichlorobenzoate[c]	105–113d.	18	32.0	31.6	31.6
p-Bromobenzoate	142–145	62	31.2	30.8	30.9
m-Bromobenzoate	84–93dec.	9	31.2	31.0	30.9
p-Iodobenzoate	152–155d.	58	28.0	27.7	27.7
m-Iodobenzoate	94–96dec.	8	28.0	27.9	27.9
p-Fluorobenzoate	158–162	50	36.8	36.8	36.7
m-Fluorobenzoate	81–84	37	36.8	36.8	36.5
o-Fluorobenzoate[d]	[b]	11	36.8	36.5	36.4
p-Methylbenzoate	118–121d.	60	37.1	37.1	37.0
Acid phthalate[e]	[b]	69	34.4	34.2	34.2
Stearate	64–66	51	25.9	25.9	25.6

[a] The success of the reaction for the synthesis of the iodine salt appears to decrease with decreasing electron withdrawing power of the ring substituents. Moreover, the yield of the desired product seems to depend upon the position of the substituent, decreasing in the order $p > m > o$. The reaction is unsuccessful when applied to acids which contain *o*-substituents exhibiting weak +I or +T effects, and to acids substituted in any position by groups, such as hydroxy and amino, which exhibit strong +T effects. [b] Decomposes over a wide range. [c] These compounds were prepared by treating the silver salts with a large excess of pyridine and less than the theoretical amount of iodine. If treated under ordinary conditions, a residue was obtained from which the acid could be isolated by extracting with Skellysolve A and removing the excess iodine with mercury. [d] This compound could not be salted out of solution, but the residue remaining after evaporation of the chloroform gave the compound after continuous washing with Skellysolve A and ether. These washings on evaporation yielded crystals identified as the acid. [e] This compound salted out of solution as a heavy, viscous liquid which crystallized on standing in the cold.

tion of sodium carbonate was added until the solution tested basic to litmus. Nitric acid was then added dropwise until the solution tested acid to litmus. Any solid present was filtered off and a hot aqueous solution of an equivalent amount of silver nitrate was added. The silver salt was removed by filtration, washed with distilled water and alcohol, and dried at 70°.

Preparation of Positive Iodine Compounds.—To a suspension of a few grams of the silver salt of the acid in dry chloroform, iodine was added with shaking until the solution remained light orange in color. A slight excess of the coördinating base was then added and the addition of iodine was continued until the solution again remained colored after shaking. The silver iodide was filtered and a volume of Skellysolve A from one to four times the volume of the solution, depending upon the solubility of the compound being prepared, was added. The solution was allowed to stand overnight in the dark and the solid which had precipitated was filtered, washed with ether (or with Skellysolve if the compound was soluble in ether), and dried *in vacuo* over sulfuric acid. The positive iodine compounds are white or pale yellow crystalline solids.

Analysis of Positive Iodine Compounds.—To a 0.05-g. sample of the iodine compound, an excess of potassium iodide solution was added. Five ml. of carbon tetrachloride was then added and the solution acidified with a few drops of acetic acid. The organic acid which separated was retained in the carbon tetrachloride layer and did not interfere with the analysis. Finally, the free iodine in the solution was titrated with a 0.01 *N* sodium thiosulfate solution.

Acknowledgment.—The authors wish to thank the Upjohn Company for their grant during the time this work was carried out.

Summary

Thirty-one new compounds of positive univalent iodine coördinated with pyridine or α- or β-picoline have been prepared.

LAWRENCE, KANSAS RECEIVED SEPTEMBER 15, 1948

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF NEW YORK UNIVERSITY]

Transference Numbers of Zinc and Cadmium Sulfates at 25°, as Functions of the Concentration

BY GERARD M. WOLTEN AND CECIL V. KING

The method of determining transference numbers by means of the ratio of the electromotive forces of concentration cells with transference to those without[1] is thought by some[2] to be capable of great accuracy.

To throw further light on this method and to provide additional data on transference numbers, we have applied this method to solutions of zinc sulfate and cadmium sulfate at 25°.

Experimental

To measure the e. m. f.'s of zinc and cadmium sulfate concentration cells with transference, of the type MHg, $MSO_4(m')$, $MSO_4(m'')$, MHg, where MHg indicates an amalgam, we used a cell of the same design as used by Stokes and Levien.[3] A Leeds and Northrup type K-1 potentiometer and a no. 2500B galvanometer, with 8000 to 10,000 ohms in series for suitable damping, were used. To shield against electric leakage and stray currents, the equipotential shielding method of White[4] was used. The thermostat was kept at 25.00 ± 0.02°. All cells reached equilibrium within one hour and stayed constant for at least several hours. Duplicate cells were reproducible within 0.05 mv., each cell being constant within 0.03 mv. or better.

Materials

Zinc, zinc sulfate, and cadmium sulfate were the "C. P. Analysed" reagent grade of the J. T. Baker Chemical Co. C. P. triply distilled mercury was obtained from F. W. Berk & Co. Cadmium was obtained from the Udylite Corp. and by spectrographic analysis shown to be 99.95%

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(1) Harned and Dreby, THIS JOURNAL, **61**, 3113 (1939).

(2) Taylor and Taylor, "Elementary Physical Chemistry," 3rd ed., D. Van Nostrand Co., New York, N. Y., 1942, p. 388.

(3) Stokes and Levien, THIS JOURNAL, **68**, 333 (1946).

(4) White, *ibid.*, **36**, 2011 (1914).