tion state. This type of mechanism should be favored by the same type of structures which increase the stability of free radicals and experiments are in progress to establish such cases. The catalysis of certain *cis–trans* isomerizations by atoms most probably proceeds by such a mechanism.

Summary

1. It has been shown that the same base is obtained upon half-reduction of both *cis* and *trans* isomers of 4,4′-dinitrostilbene.

2. Two salts of this base have been prepared and it is suggested that they are the geometric isomers of the salts.

3. It has been demonstrated by spectroscopic means that the salts in acidified alcohol exist in both forms in comparatively rapid equilibrium with each other and that this equilibrium can be easily shifted by acid. The *cis–trans* equilibrium is maintained by virtue of the equilibrium between the ion and the base.

4. The significance of the resonance phenomenon in understanding the effects of groups on the ease of rotation about a double bond is indicated.

BERKELEY, CALIF. RECEIVED SEPTEMBER 9, 1940

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE STATE UNIVERSITY OF IOWA]

Iodine Monochloride. III. The Systems Iodine Monochloride–Acetic Acid and Iodine Monochloride–Carbon Tetrachloride[1]

BY JACOB CORNOG AND LEONARD E. OLSON

In an earlier investigation Olson[2] learned that the cryoscopic constant of iodine monochloride decreased from 29 to 3 when the mole per cent. of carbon tetrachloride solute was increased from 0.6 to 23. The freezing point curve based on these data was shaped like the letter "S." Both the abnormally large cryoscopic constants and the rather unusual form of the freezing point curve roused our curiosity and prompted the present study of the cryoscopic preparation of solutions of iodine monochloride. Carbon tetrachloride was chosen as a non-polar, non-reactive solute, and acetic acid as a somewhat polar solute.

The System Iodine Monochloride–Acetic Acid

Materials: Acetic acid of reagent quality was purified by repeated recrystallizations until the freezing point rose to 16.40°.

Iodine monochloride was prepared by the method of Cornog and Karges,[3] and was redistilled in the Cornog and Olson[4] "sublimer." Thus prepared it had a freezing point of 27.3°, which is 0.1° higher than any previously published value.

Procedure.—Glass-stoppered flasks containing mixtures of iodine monochloride and acetic acid were suspended in a thermostat in which the maximum temperature variation was ±0.1°. The temperature of the thermostat and the composition of the mixtures were so regulated that partial freezing occurred. After intervals of from eight to ten days, a pipet was used to remove portions of the liquid phase for analysis. Equilibrium between the solid and liquid phases was assumed to exist when the analyses of successive portions checked within 2%. The temperature of the thermostat was then changed and the routine was repeated. Data thus obtained are shown in Table I and are graphically represented in Fig. 1. The approximate composition and freezing point of the eutectic indicated in Fig. 1 was determined by extending the freezing point curves till they intersected. The location of this eutectic was experimentally verified by determining the freezing point of a mixture having approximately the indicated composition.

TABLE I

COMPOSITION OF THE LIQUID PHASE IN EQUILIBRIUM WITH THE SOLID PHASE

Solid phase–iodine monochloride		Solid phase–acetic acid	
Temp., °C.	Mole per cent.[a] acetic acid	Temp., °C.	Mole per cent.[a] acetic acid
27.3	0.00	16.4	100.0
26.0	4.9	10.2	91.3
25.0	7.3	0.1	82.2
23.0	12.8	−18.2	68.4
20.0	17.8		
19.0	19.6	Eutectic	
17.0	24.0		
15.0	26.7	−35.5	60.0
10.0	34.3		
0.1	42.1		
−18.2	53.2		

[a] Each value in this column represents averages of two or more analyses agreeing within 1.5%.

It can be seen from these data that this system is a simple binary one in which each com-

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[1] This paper is an excerpt from the Ph.D. thesis of Mr. Leonard E. Olson, State University of Iowa (1940).

[2] Olson, unpublished M.S. thesis, University of Iowa (1936).

[3] Cornog and Karges, "Inorganic Syntheses," Vol. 1, p. 165.

[4] Cornog and Olson, *Ind. Eng. Chem., Anal. Ed.*, **11**, 551 (1939).

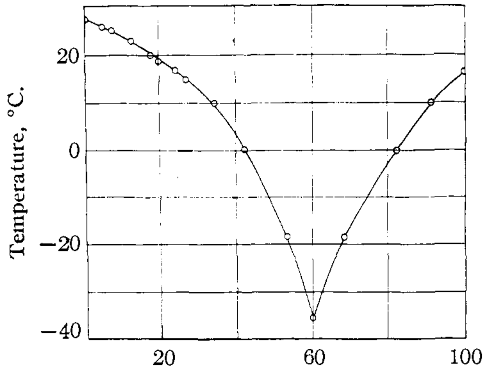

Fig. 1.—The system iodine monochloride–acetic acid temperature–composition diagram.

ponent depresses the freezing point of the other to form a eutectic with a freezing point of −35.5°, the solid phases being pure components. Incidentally, it should be observed that the freezing point of the pure iodine monochloride is 0.1° higher than any previously published value.

The System Iodine Monochloride–Carbon Tetrachloride. Materials and Procedures.—The carbon tetrachloride used boiled within less than 2° and froze at −22.7°. Four different procedures were employed in the measurements, which can best be described in connection with Fig. 3 as follows. A. This was used in obtaining the data shown on curve A above 0° and was the same procedure as employed in the measurements of the system iodine monochloride–acetic acid. B. The data of curve AB below 0° and all of the data of curve AD were obtained by partly freezing iodine monochloride–carbon tetrachloride mixtures in chamber A of the vessel represented by Fig. 2. The partly frozen mixture was maintained at a temperature constant to ±0.1° till equilibrium had been reached between the solid and liquid phases, after which the vessel was inverted, when the liquid phase drained into chamber C leaving the solid phase in chamber A. C. The composition and freezing point of the eutectic represented by B and the location curve BC, Fig. 3, were established from the cooling curves of iodine monochloride–carbon tetrachloride mixtures of known composition. No effort was made to determine the composition of the solid phase which separated in this connection. D. The location of the curve EFG, Fig. 3, was determined by undercooling iodine monochloride–carbon tetrachloride mixtures in a thermostat, then removing and analyzing portions of the double layers which formed.

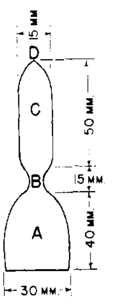

Fig. 2.—Vessel used in procedure B to obtain and separate solid and liquid phases from partly frozen iodine monochloride–carbon tetrachloride mixtures.

The data recorded in Table II are represented graphically in Fig. 3.

TABLE II

TEMPERATURE–COMPOSITION RELATIONS IN SYSTEM IODINE MONOCHLORIDE–CARBON TETRACHLORIDE

Temp., °C.	Concn. CCl_4, mole %	Temp., °C.	Conc. CCl_4, mole % Liquid	Solid
Procedure A			Procedure B	
27.3	0.0	23.1	..	0.85
26.0	2.0	18.8	..	4.1
25.0	3.9	10.2	..	15.3
23.0	9.4	0.1	90.7	29.3
22.0	15.1	− 8.0	93.2	38.5
21.0	24.3	−15.7	95.3	..
20.5	43.2			
20.0	54.0		Procedure C	
19.0	64.6			Eutectic
17.0	73.2	−25.5		98.7
15.0	78.4	−26.4		98.2
10.0	85.2		Procedure D	
0.0	90.7		Upper layer	Lower layer
		0.0	76.2	15.3
		10.0	65.6	29.5

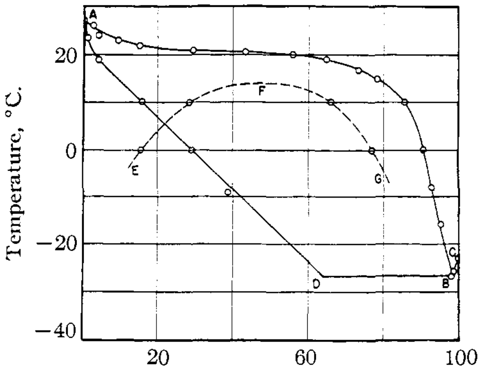

Fig. 3.—The system iodine monochloride–carbon tetrachloride.

These data show that the system iodine monochloride–carbon tetrachloride consists of a series of solid solutions of which the liquidus is represented by the S-shaped curve AB and the solidus is represented by the curve AD. A eutectic represented by B having a freezing point −26.4° and containing 98.2 mole per cent. carbon tetrachloride is formed between the solid solutions and another solid phase of undetermined composition. The components also form a metastable double layer liquid system, represented by curve EFG, having a critical temperature approximately 14°.

The literature of chemistry contains many reports of different types of systems of solid solutions none of which, so far as the authors know, display S-shaped liquidus curves. Likewise a search of the literature discloses that a number of investigators[5,6,7,8,9,10,11,12] have studied metastable double layer liquid systems and obtained S-shaped freezing point curves similar to the present one, but, with the possible exception of Faucon,[9] these investigators fail to mention the identity of the solid phases associated with the systems studied. Had they done so, perhaps, some of the systems would also be found to contain both solid solutions and metastable double layers.

Summary

1. The system iodine monochloride–acetic acid is a simple binary system in which each component depresses the freezing point of the other till a eutectic is formed.

2. The system iodine monochloride–acetic acid forms a series of solid solutions of which the liquidus is represented by an S-shaped curve. A eutectic is formed between the solid solutions and a solid phase of undetermined composition. The components also form a metastable double layer liquid system.

3. Iodine monochloride prepared for use in these researches had a freezing point 0.1° higher than the currently accepted value.

IOWA CITY, IOWA RECEIVED JULY 5, 1940

(5) Alexjew, *Wied. Ann.*, **28**, 305 (1886).

(6) Roozeboom, *Rec. trav. chim.*, **8**, 257 (1889).

(7) Flaschner, *J. Chem. Soc.*, **95**, 668 (1909).

(8) Coehn, *Chem. Weekblad*, **7**, 277 (1910).

(9) Faucon, *Ann. chim.*, **8**, 19, 70 (1910).

(10) Baume and Georgitses, *J. chim. phys.*, **12**, 250 (1914).

(11) Sidgwick and Ewbank, *J. Chem. Soc.*, **119**, 979 (1921).

(12) Bond and Beach, THIS JOURNAL, **48**, 348 (1926).

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF PURDUE UNIVERSITY]

The Potential of the Yb^{+++}-Yb^{++} Electrode

BY GEORGE C. WALTERS[1] AND D. W. PEARCE

The determination of the oxidation potentials of the "anomalous" divalent ions of the rare earths is attended with difficulty due to the instability of these ions,[2] which react more or less rapidly with water or with H^+ thus

$$2Yb^{++} + 2H^+ \longrightarrow H_2 + 2Yb^{+++}$$

Because of this difficulty, as well as because of the rarity of certain of the elements involved, few quantitative data concerning the relative stability[3] of these ions are available. Due to the ready coöperation of Professor B. S. Hopkins of the University of Illinois a sample of purified Yb_2O_3, earlier prepared[4] by one of us, was kindly placed at our disposal. We wish to take this opportunity to thank Professor Hopkins for this favor.

The method used for the determination was very similar to that applied by McCoy[5] in his work with the somewhat more stable (E^0 = 0.43 v.) Eu^{++} ion. In general, the method consisted in first reducing electrolytically, to a predetermined extent, a solution of the trivalent ion to the divalent condition; an additional known amount of the trivalent ion was then added and a switch thrown to stop electrolysis and to cut into a prepared potentiometer circuit the set of auxiliary electrodes already dipping into the solution and into a standard half cell. Preliminary experiments were used to determine the approximate[6] potentiometer setting so that in the later runs only a matter of seconds for the final accurate adjustment was required.

Materials.—The chemicals used in the various analytical and electrochemical operations, sodium thiosulfate, glacial acetic acid, iodine, sodium oxalate, potassium permanganate, potassium chloride and oxalic acid, were of the C. P. or A. R. grade. Reagents and solutions were standardized by recognized standard procedures. The water was ordinary distilled water redistilled from alkaline permanganate solution.

The ytterbium sesquioxide was analyzed spectrographically and found to contain a trace of lutecium and a considerable amount of lanthanum. The atomic weight of the mixture was determined using a modified oxalate to oxide, oxalate to permanganate method.[7] This yielded the result 171.025 as the average of 172.06, 171.94, 172.13, 171.96. Disregarding the trace of lutecium present, this average gave by calculation a purity of 96.33% Yb_2O_3 (by weight) for the mixture. The ytterbic acetate solutions were prepared by dissolving weighed amounts of this oxide, previously ignited to constant weight, in hot glacial

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[1] Part of a thesis to be submitted by George C. Walters to the Graduate School of Purdue University in partial fulfillment of the requirements for the degree of Master of Science in Chemistry.

[2] Pearce and Selwood, *J. Chem. Education*, **13**, 224–230 (1936).

[3] Pearce, *Chem. Rev.*, **16**, 121–147 (1935).

[4] Pearce, Naeser and Hopkins, *Trans. Electrochem. Soc.*, **69**, 557–565 (1936).

[5] McCoy, THIS JOURNAL, **58**, 1578 (1936).

[6] Latimer, "Oxidation Potentials," Prentice-Hall, Inc., New York, N. Y., 1938, p. 269, estimated the potential of the couple at 0.6 v.

[7] Russell and Pearce, forthcoming publication.