hexane were isolated in small amounts and identified by comparison with authentic samples prepared by the method of Baldock, Levy and Scaife[4] from cyclohexene and nitrogen tetroxide.

Reaction of the Complex with Methyl Acrylate.—Methyl acrylate, 58.6 g. (0.68 mole) in 93 g. of CCl_4 was added slowly to 160 g. (1.0 mole) of complex in 322 g. of CCl_4 during 1.5 hours at 0° while oxygen gas was bubbled into the mixture. The product was allowed to warm up to room temperature and to stand overnight. It was decomposed with ice and water and 101 g. of urea. The lower layer was separated, washed with water till neutral, dried and fractionally distilled. There were obtained 1.38 g. (1.5% theory) of methyl 3-nitroacrylate, b.p. 36–40° (1 mm.), freezing point 33°; and 3.91 g. (3.8% theory) of methyl 3-nitro-2-hydroxypropionate, b.p. 86–89° (1 mm.), glassy at −70°. Other unidentified products including a polymer were also present.

Reaction of the Complex with Naphthalene.—A slurry of 80 g. (0.50 mole) of the complex in 200 ml. of nitroethane was cooled to ice temperature. A solution of naphthalene, 30 g. (0.234 mole), in 200 ml. of nitroethane also cooled to 0° was added dropwise to the flask with rapid stirring. The mixture developed a light yellow-green color during the final stages of the addition. Stirring was continued at ice temperatures for 5 hr., then the mixture was allowed to stand 24 hours at ice temperatures. Finally the reaction mixture was heated gently for 3 hours, cooled and poured into a mixture of ice and water to destroy the complex. Again the water layer became blue in color. The non-aqueous layer was separated, dried and the nitroethane solvent removed by distillation. The residue solidified on cooling and weighed 36.5 g. (65% theory calcd. as dinitronaphthalenes).

Anal. Calcd. for $C_{10}H_6N_2O_4$: N, 12.81. Found: N, 13.00.

Following the separation procedure of Hodgson and Turner[8] the product was partially reduced with sodium sulfide and sulfur to a mixture of 1,8-dinitronaphthalene, 13.2 g., m.p. 171°, and 5-nitro-1-naphthylamine, soluble in acid, 19.8 g., m.p. 119°. From this it may be calculated that the ratio of dinitronaphthalenes formed was 1,8-/1,5- = 36.5/63.5.

Acknowledgment.—We are indebted to the Office of Naval Research for the financial support of part of this work.

[8] H. H. Hodgson and H. S. Turner, *J. Chem. Soc.*, 318 (1943).

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Quinoline Derivatives of Iodine(I)

BY ERVIN COLTON

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The positive character of the halogens is well established,[1] and the cationic nature of iodine is almost to be expected from its metallic-like appearance and its position in the periodic classification.

Carlsohn[2] and his students pioneered in the field of coördination compounds of unipositive iodine. These investigators were able to stabilize a number of salts of the hypothetical base, IOH, by coördination with organic tertiary amines. The general method of preparation is illustrated by the following equation, the calculated amounts of material being brought together in some non-aqueous medium, usually chloroform.

$$AgNO_3 + 2C_5H_5N + I_2 \longrightarrow I(C_5H_5N)_2NO_3 + AgI$$

The mercurous salt can also be used as a starting material for obtaining unipositive iodine complexes. In this case, benzene appears to be the best medium for effecting reaction.

$$(RCOO)_2Hg_2 + 3I_2 + 6C_5H_5N \longrightarrow 2RCOOI{\cdot}C_5H_5N + 2HgI_2{\cdot}(C_5H_5N)_2$$

(R = aromatic group)

A series of unipositive iodine derivatives of carboxylic acids, with pyridine, α- and β-picoline as coördinating agents, has been reported.[3,4] This paper reports the preparation of some compounds of iodine(I) coördinated with quinoline.

Experimental

Materials.—The iodine used was J. T. Baker C.P. grade. It was stored in a desiccator over phosphoric anhydride. Eastman Kodak Co. white label quinoline was placed over potassium hydroxide pellets for two weeks and then distilled twice through a 30″ fractionating column, the middle cut boiling at 234° at 732.1 mm. being collected. The acids were Eastman Kodak Co. white label products and were recrystallized prior to use. All solvents were dried and distilled before use.

Procedure.—The silver salts were prepared by dissolving a known weight of acid in 95% ethanol, with slight heating if necessary, and then adding aqueous sodium carbonate until the solution tested just basic to litmus. Dilute nitric acid was then added until the solution tested just acid to litmus, and any organic acid precipitating at this point was removed. A solution of silver nitrate containing a quantity of silver equivalent to the amount of organic acid used was added, and a heavy white precipitate of the silver salt of the acid formed. The white solid was allowed to settle, removed by filtration, washed well with 95% ethanol, and dried at 70° for 24 hours before use.

The method of preparation of the derivatives of iodine(I) is similar for all acids and that for *p*-bromobenzoic acid will be given in detail. Exactly 9.6 g. of silver *p*-bromobenzoate was suspended in 100 ml. of dry chloroform. While the suspension was shaken continuously, iodine and quinoline were added alternately in small portions until 8 g. of the former and 4 g. of the latter had been introduced. A reaction began immediately, and silver iodide precipitated. After 25 minutes of continuous shaking, 50 ml. of chloroform was added to dilute the reaction mixture. The heavy precipitate of silver iodide was removed by filtration, and 500 ml. of low boiling petroleum ether was added to the filtrate. A large quantity of crystals formed at once. After 30 minutes, the crystalline product was collected on a filter and washed with petroleum ether and dry diethyl ether and then dried *in vacuo* over sulfuric acid for 24 hours. The yield was 9.7 g., 68% of theoretical, based on the amount of silver salt employed. The sparkling light yellow crystals decomposed at 139–143°, uncor.

$$p\text{-}BrC_6H_4COOAg + I_2 + C_9H_7N \longrightarrow p\text{-}BrC_6H_4COOI{\cdot}C_9H_7N + AgI$$

TABLE I

DERIVATIVES OF MONOQUINOLINE IODINE(I)

Salt[a]	Yield, %	Decomp. range, °C.[b]	% Iodine Calcd.	% Iodine Found
Benzoate	73.4	141–150	33.7	33.6, 33.5
p-Bromobenzoate	68.0	139–143	27.8	27.8, 27.8
m-Chlorobenzoate	60.8	121–124	30.8	30.7, 30.6
p-Chlorobenzoate	76.8	136–141	30.8	30.3, 30.5
o-Chlorobenzoate	38.4	129–133	30.8	30.8, 30.6
o-Iodobenzoate	43.1	110–113	25.3	25.4, 25.2
m-Iodobenzoate	75.3	125–133	25.3	25.0, 25.3
o-Nitrobenzoate	71.1	122–127	30.1	30.1, 30.2
m-Nitrobenzoate	23.8	160–181[c]	30.1	29.8, 29.7

[a] All salts were pale yellow or golden. [b] Uncorrected. [c] This compound began to turn pink at 160° and was completely decomposed at 181°.

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[1] J. Kleinberg, *J. Chem. Ed.*, **23**, 559 (1946).

[2] H. Carlsohn, "Über eine neue Klasse von Verbindungen des einwertigen Iods," Verlag Hirzel, Leipzig, 1932.

[3] R. A. Zingaro, J. E. Goodrich, J. Kleinberg and C. A. VanderWerf, THIS JOURNAL, **71**, 575 (1949).

[4] R. A. Zingaro, C. A. VanderWerf and J. Kleinberg, *ibid.*, **72**, 5341 (1950).

Analysis.—The compound was analyzed by weighing a sample into an erlenmeyer flask and then adding acidified potassium iodide solution, the liberated iodine being determined with standard sodium thiosulfate solution.[3]

$$I^+ + I^- \longrightarrow I_2$$

The results of this investigation are shown in Table I.

Acknowledgment.—The author is indebted to Dr. Jacob Kleinberg for guidance in this investigation.

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The Effect of Water and of Glycerol on the Decarboxylation of Oxalic Acid

BY LOUIS WATTS CLARK

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It has long been known that oxalic acid is readily decomposed by heat, yielding formic acid and carbon dioxide.[1] Well known also is the fact that decarboxylation of oxalic acid takes place in glycerol.[2] Up to the present time, however, quantitative data on the reaction have not been available. The results of kinetic studies on this reaction which have been made in this Laboratory are reported herein.

Experimental

Reagents.—Oxalic Acid Anhydrous, Analytical Reagent Grade, Oxalic Acid Dihydrate, Analytical Reagent Grade, and Glycerol, Analytical Reagent Grade, 95% by volume, were used in these experiments.

Apparatus.—The experiments described in this paper were carried out in an apparatus similar to that used by the author in studying the decomposition of trichloroacetic acid alone and in glycerol.[3]

Effect of Glycerol on the Decomposition of Oxalic Acid.—In studying the effect of glycerol on the decomposition of oxalic acid, 0.1607 g. of anhydrous oxalic acid (sufficient to yield 40.0 ml. of carbon dioxide at STP on complete reaction) was weighed into a paper thin glass capsule. The sample was introduced in the usual manner into the reaction flask containing 100 ml. of glycerol, and the evolved gas was collected and measured. The volumes of gas evolved with time at five different temperatures are shown in Fig. 1.

Effect of Water on the Decomposition of Oxalic Acid.—Oxalic acid dihydrate decomposes at a measurable rate when heated to its melting point (101.5°) and above when a sufficient quantity of the acid (at least one mole) is used. If additional water is added to the molten dihydrate the reaction slows down. However, the rate can still be measured even when six moles of water per mole of acid is present. A straight line is obtained when the logarithm of the rate is plotted against moles of water.

In studying the effect of water on the decomposition of oxalic acid, one mole (126.06 g.) of the dihydrate was weighed into the reaction flask which was placed in the constant temperature oil-bath. The acid quickly melted, the mercury sealed stirrer was started, and the evolved carbon dioxide was collected and measured in the usual manner. This, of course, gave the effect of two moles of water on the decomposition of the acid at the particular temperature concerned. To obtain the effect of three, four, five and six moles of water per mole of oxalic acid the procedure was exactly the same, except that in addition to the mole of dihydrate, one, two, three and four moles, respectively, of distilled water was introduced into the reaction flask before inserting it in the oil-bath. When all the data at one temperature had been collected and checked for reproducibility the oil-bath temperature was raised and the procedure repeated at a higher temperature. The data thus obtained at four different temperatures are shown graphically in Fig. 2.

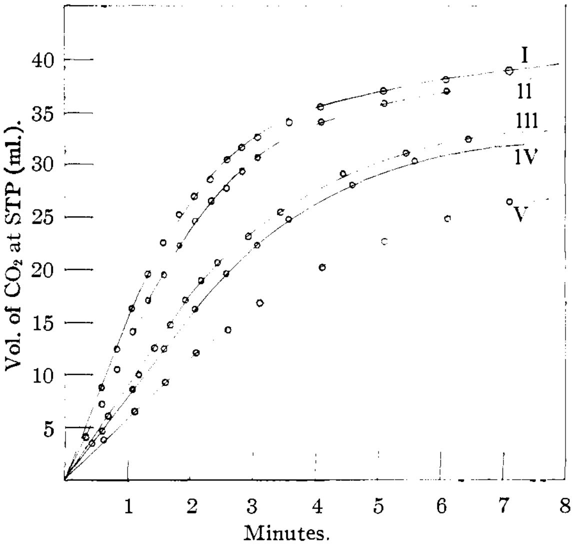

Fig. 1.—Volume of CO_2 (at STP) evolved with time at different temperatures, using 0.1607-g. samples of anhydrous oxalic acid in 100 ml. of glycerol: I, 158.2°; II, 154.2°; III, 148.2°; IV, 145.9°; V, 139.5°.

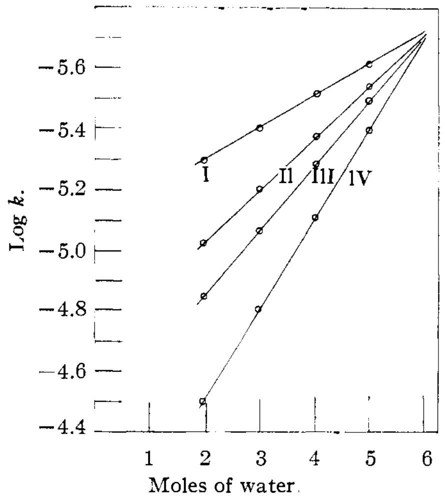

Fig. 2.—Effect of water on the decarboxylation of oxalic acid at different temperatures: I, 117.1°; II, 121.8°; III, 124.8°; IV, 130.8°.

Results and Discussion

The Reaction in Glycerol.—In glycerol it was found that the stoichiometric amount of carbon dioxide was not obtained in every experiment. For example, at 123.6°, the final observed volume of carbon dioxide collected (corrected to STP) was 24.6 ml.; at 132.4°, 32.6 ml.; at 139.5°, 33.3 ml.; at 145.9°, 35.4 ml.; at 150.1°, 37.8 ml.; at 151.8°, 38.6 ml.; at 154.2°, 38.7 ml.; at 156.2°, 40.0 ml.; at 158.2°, 39.4 ml.

It is seen from these data that the decomposition of oxalic acid in glycerol is not stoichiometric at temperatures below 150°. Above 150°, however, the reaction appears to be practically quantitative, considering the limit of error of the experiment and the limitations of the ideal gas law.

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[1] H. J. Lucas, "Organic Chemistry," American Book Co., New York, N. Y., 2nd Ed., 1953, p. 190.

[2] Reference 1, p. 250.

[3] L. W. Clark, THIS JOURNAL, **77**, 3130 (1955).