

# Notes

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## Synthesis and Properties of Triiodoacetic Acid and Its Salts

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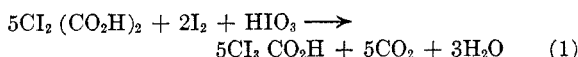
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In 1893, Angeli reported<sup>1</sup> that the reaction between iodic acid and malonic acid gave triiodoacetic acid and diiodoacetic acid in unspecified amounts. The same method was used in 1938 to prepare the triiodo compound, but no experimental details were given.<sup>2</sup> Recently it was reported that nitrogen triiodide and acetoacetic ester yielded a material thought to be a mixture of diiodoacetamide and triiodoacetamide.<sup>3</sup> In connection with the preparation of triiodoacetic acid for use in another investigation, the reaction of malonic acid with iodic acid has been reexamined, and attempts have been made to determine the conditions which will give optimum yields of triiodoacetic acid.

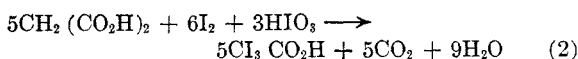
Under the conditions specified by Angeli,<sup>1</sup> the predominant product is diiodoacetic acid. We have found that the ratio of products (diiodoacetic and triiodoacetic acids) is dependent on the initial ratio of iodic acid to malonic acid. Triiodoacetic acid can be obtained as the major product, in yields of 50–60% based on iodic acid, if an iodic to malonic acid weight ratio of 1.5 is used. Diiodoacetic acid was the major product with reactant weight ratios of less than about 1.2, and the only product isolated when a ratio of 0.6 was used. With reactant weight ratios higher than 1.5, crystallization of triiodoacetic acid from the reaction mixture was accompanied by precipitation of increasingly larger amounts of free iodine. A reactant ratio of 2.0 gave a heavy precipitate of free iodine, and no triiodoacetic acid was isolated. The stability of triiodoacetic acid is involved here, since it was found that it decomposes to free iodine in the presence of concentrated aqueous iodic acid.

The steps in the reaction that lead to the observed products have not been clearly defined. Angeli<sup>1</sup> assumed that the first step in the reaction was formation of diiodomalonic acid, which could react further by simple decarboxylation to yield diiodoacetic acid or by decarboxylation and iodination to give triiodoacetic acid. Willstätter<sup>4</sup> has prepared diiodomalonic acid by the reaction of malonic acid

with iodic acid and iodine in anhydrous formic acid as a solvent and noted that it is unstable in water. We obtained a 30% yield of triiodoacetic acid from the reaction of diiodomalonic acid with a suspension of iodine in aqueous iodic acid using charge weights based on Equation 1. The possibility that the use of



free iodine in the reaction of malonic acid with aqueous iodic acid (Equation 2) would lead to higher yields of triiodoacetic acid was also explored. Good



yields of triiodoacetic acid were obtained by this method, but the product was contaminated by large amounts of unreacted iodine.

Crystalline triiodoacetic acid was found to be quite stable at room temperature, in contrast to a report<sup>2</sup> that decomposition is rapid. The acid decomposes rapidly at higher temperatures, however. Triiodoacetic acid is very soluble in polar organic solvents, but the solutions as a rule are extremely unstable, rapidly developing an iodine coloration. In certain solvents as noted in the experimental section, the acid is stable enough to permit further work, if done rapidly. Triiodoacetic acid is insoluble in water, but aqueous suspensions are quite stable. It is soluble, with rapid decomposition, in dilute (4%) sodium hydroxide, but in more concentrated sodium hydroxide (10–40%) the acid is insoluble and little decomposition is observed. The acid may be partially recovered by rapidly neutralizing a freshly prepared bicarbonate solution.

The lead and sodium salts of triiodoacetic acid were prepared and isolated. Attempts to isolate a calcium salt were unsuccessful, although the calcium salt of diiodoacetic acid was prepared.

### EXPERIMENTAL<sup>5</sup>

*Triiodoacetic acid.* A solution of 20 g. of malonic acid in 30 cc. of water was added to an almost boiling solution of 30 g. of iodic acid in 80 cc. of water. The resulting solution was cautiously heated until the evolution of carbon dioxide was vigorous and then cooled immediately by plunging the flask into an ice bath; several small pieces of ice were added to the solution to help moderate the reaction.<sup>6</sup> After the reaction had subsided, the yellow reaction mixture was allowed to stand at room temperature. There was a mildly exothermic reaction, the temperature rising to about 45° with a steady evolution of gas; in about 1.5 hr., the reaction solution was a

(1) A. Angeli, *Ber.*, **26**, 595 (1893).

(2) R. A. Fairclough, *J. Chem. Soc.*, 1186 (1938).

(3) J. F. Fellman, S. H. Wilen, and C. A. VanderWerf, *J. Org. Chem.*, **29**, 713 (1956).

(4) R. Willstätter, *Ber.*, **35**, 1374 (1902).

(5) All melting points are uncorrected.

(6) Particular care must be taken in the heating step, as the reaction may very easily get out of hand and become uncontrollably violent.

bright yellow-orange color. Triiodoacetic acid as golden yellow crystals settled out and was filtered after another hour. Air drying the product served also to remove a small amount of free iodine which was present. Weight 14.3 g. (57.6%), m.p. 135–140° (dec.); reported m.p. 150° (dec.).<sup>1</sup> Other samples of triiodoacetic acid prepared in this manner gave m.p.'s as high as 150–154° (dec.).

*Anal.* Calcd. for C<sub>2</sub>H<sub>2</sub>O<sub>2</sub>I<sub>3</sub>: I, 86.97%; eq. wt. 438. Found: I, 87.5%; eq. wt.<sup>7</sup> 449.

After removal of the triiodoacetic acid, the mother liquor became a dark color and deposited 1.2 g. of iodine; this was removed. By concentration of the solution, a total of 5.4 g. (20.3%) of diiodoacetic acid was isolated as pale yellow needles, m.p. 110–111°; reported<sup>1</sup> m.p. 110°. It was recrystallized from chloroform. Data obtained by varying the reactant ratio were as follows:

Weight Ratio HIO <sub>3</sub> /Malonic Acid	Yield, Wt. %	% Based on Iodine in HIO <sub>3</sub>	
		Cl <sub>3</sub> COOH	CHI <sub>2</sub> COOH
0.60	0		58.6
1.00	19.2		51.8
1.00 <sup>a</sup>	39.6		—
1.00 <sup>a</sup>	26.4		—
1.26	37.2		30.4
1.50	46.8		28.2
1.50	57.6		20.3
1.50 <sup>a</sup>	51.6		28.2
1.75	22.8		21.4
2.00 <sup>a,b</sup>	0		14.7

<sup>a</sup> Reaction mixture was kept cold after the initial reaction.

<sup>b</sup> A trace of a white solid, m.p. 300°, was isolated.

*Diiodomalonic acid.* Diiodomalonic acid was prepared by the method of Willstätter.<sup>4</sup> A mixture of 10 g. (0.167 mole) of malonic acid, 6.8 g. (0.10 mole) of iodic acid, and 19.6 g. (0.20 mole) of finely divided iodine in 50 cc. of 90% formic acid was stirred at room temperature 3 hr. The reaction mixture was allowed to stand overnight in a refrigerator and then filtered while cold. The product was dried on a clay plate to allow excess iodine to evaporate, giving 20 g. (58%) of diiodomalonic acid as pale yellow crystals, m.p. 110° (dec.); reported m.p. 119–120° (dec.).<sup>4</sup>

*Conversion of diiodomalonic acid to triiodoacetic acid.* Ten g. of diiodomalonic acid was added to 20 cc. of water containing 1.0 g. of iodic acid and 2.85 g. of pulverized iodine. The mixture was allowed to stand at room temperature with frequent shaking for 3 hr. A pale yellow solid appeared almost immediately. After standing overnight, the mixture was filtered and the product air-dried 6 days to remove free iodine, giving 3.7 g. (30%) of triiodoacetic acid, m.p. 140–142° (dec.).

*Anal.* Calcd. for C<sub>2</sub>H<sub>2</sub>O<sub>2</sub>I<sub>3</sub>: eq. wt. 438. Found: eq. wt. 450, 439.

*Reaction of malonic acid with iodine and iodic acid.* A mixture of 10.0 g. (0.096 mole) of malonic acid, 29.3 g. (0.115 mole) of pulverized iodine, and 10.2 g. (0.058 mole) of iodic acid in 250 cc. of water was stirred vigorously. After about 20 min., a yellow solid appeared; in another 15–20 min., evolution of carbon dioxide started with considerable foaming. The reaction was slightly exothermic; the temperature was not allowed to exceed 45° by using a water bath when necessary. A heavy yellow solid appeared after 3.5 hr. After standing overnight in a refrigerator, stirring was resumed for 3 hr. at room temperature. The mixture was filtered and the yellow solid dried on a clay plate in the air to remove excess iodine, giving 17.5 g. (42%, based on malonic acid) of

the triiodoacetic acid, m.p. 131–132° (dec.). Other samples of the acid prepared in this manner had m.p. as high as 154–155° (dec.).

*Anal.* Calcd. for C<sub>2</sub>H<sub>2</sub>O<sub>2</sub>I<sub>3</sub>: I, 86.9%. Found: I, 86.4%.

After removal of the triiodoacetic acid, concentration of the mother liquors gave about 7 g. (16%) of diiodoacetic acid, m.p. 108–109° after recrystallization from chloroform.

*Preparation of salts of triiodoacetic acid. Calcium salt.* A solution of 0.25 g. of calcium acetate in 2–3 cc. of water was added to a freshly prepared solution of 1.00 g. of triiodoacetic acid in 5 cc. of dimethylformamide. Immediately a golden orange solid appeared, accompanied by evolution of a gas. After cooling in an ice bath, the solid was filtered. It decomposed on the filter paper. Similar results were obtained with acetic acid and with a carefully neutralized bicarbonate solution.

*Lead salt:* A solution of 2.0 g. of lead acetate in 10 cc. of water was added to a freshly prepared solution of 5.0 g. of triiodoacetic acid in 20 cc. of dioxane. After an induction period of a few seconds, a heavy bright yellow solid appeared. This was filtered and washed well with cold water. Drying on the filter in the air for 2 hr. did not change the color of the product. The salt was dried *in vacuo* over phosphorus pentoxide for 4 hr.; 5.1 g. of a light yellow tan product was obtained. On heating in a capillary tube, the product liberated iodine above 90° particularly at 130–140° to 180°, yielding a yellow solid which was stable at 260°.

*Sodium salt:* Two grams of triiodoacetic acid was dissolved in a solution of 0.4 g. of sodium bicarbonate in 10 cc. of water. Immediately 4 g. of sodium acetate was added to salt out the product and beautiful golden yellow, glistening leaves settled out. These were filtered and air dried, wt. 2.1 g. Upon heating in a melting point tube, the solid started losing iodine at 90°, darkened gradually from 170–180°, and became quite dark colored at 230°. The salt appeared to be relatively stable to air at room temperature.

*Preparation of calcium diiodoacetate.* Treatment of diiodoacetic acid solution in the same manner as afforded the calcium salts of triiodoacetic acid gave none of the desired salt. It was observed that the salts were more water soluble than the parent acid. Calcium diiodoacetate was obtained as a pale yellow solid in the following manner. Six g. of the acid in 10 cc. of warm water gave a two-phase liquid system. This was neutralized with 1 g. of calcium carbonate. The two layers disappeared and a clear solution resulted until the neutralization point was almost reached, then the calcium salt started crystallizing. Water was added and excess carbonate was filtered off. The solution was concentrated under reduced pressure to 5–10 cc. and cooled to give 4.9 g. of the calcium diiodoacetate, dec. above 200° with liberation of iodine.

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## Infrared Analysis of a Cyclopropane Polymer

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In 1939, C. S. Marvel and co-workers reported<sup>2</sup> the preparation of a polymer containing cyclopropane rings by dehalogenation of polyvinyl chloride with zinc.

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(2) C. S. Marvel, J. H. Sample, and M. F. Roy, *J. Am. Chem. Soc.*, **61**, 3241 (1939).

(7) After allowing a sample of the acid to stand several weeks at room temperature, the eq. wt. was redetermined and found to be 451.