

DETERMINATION OF IODOFORM BY PHOTO-OXIDATION IN ARTIFICIAL LIGHT

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A procedure for the determination of iodoform is described. It is based on the rapid decomposition of iodoform into free iodine when exposed to artificial light of mercury vapour lamp. All the three atoms of iodine are quantitatively oxidised and the free iodine has been evaluated by thiosulphate. The maximum amount of iodoform estimated by this method is 0.1 g. The analytical precision is 1% or better.

Iodoform absorbs light in the visible region (Ellis, Wells and Heyroth, "Chemical Action of Ultraviolet Light", 1941, p. 395). Ernschwiler (*Bull. Soc. Chim.*, 1939, 6, 551) observed the formation of iodine pentoxide on photo-oxidation. He subsequently attributed the formation of iodine pentoxide to the secondary reaction, the primary product of photo-oxidation being free iodine (*Compt. rend.*, 1938, 207, 1201). Bose developed a procedure (*Anal. Chem.*, 1958, 30, 1137) for the evaluation of iodoform involving its quantitative decomposition into free iodine, when a solution in ether-benzene mixture was exposed to bright sunlight. As sunlight is not always available in the laboratory the present work, using artificial light from a 80 watts mercury vapour lamp, has been undertaken.

EXPERIMENTAL

Sodium thiosulphate, iodine, and starch used were of A.R. quality. Potassium iodide and iodoform were of Merck's chemically pure variety. The following solutions were prepared: 0.02 *N*-I₂, 0.1 *N* and 0.02 *N* thiosulphate, and 1% aqueous starch.

Effect of Solvent on Photo-oxidation of Iodoform by Mercury Vapour Lamp

To find a suitable solvent for iodoform, the effect of various solvents on the process of photo-oxidation in artificial light was investigated. 0.05% Iodoform solutions were prepared in ether, benzene, chloroform, and CCl₄ and 100 c.c. of each was exposed to light from a mercury vapour lamp in a 250 c.c. conical flask, which was corked and swirled from time to time. The flask was kept as close to the lamp as possible (the distance between centres of the flask and the lamp was about 5"). Time of exposure was one hour after which 1 g. of solid potassium iodide and the starch solution were added, and the liberated iodine was titrated with 0.02 *N* thiosulphate solution.

TABLE I

Solvent.	Initial rate of decomposition.	Iodoform.	
		Present.	Found.
Ether	Very rapid	50.0 mg.	40.50 mg.
Benzene	Rapid	50.0	49.80
Chloroform	Slow	50.0	49.21
Carbon tetrachloride	Do	50.0	49.28

(1 c.c. of 0.02 *N* thiosulphate soln. \equiv 2.626 mg. of iodoform)

In ether solution the decomposition was initially very rapid, but the solution soon developed a brownish red colour, and the decomposition of iodoform was not carried to completion as the red colour of the solution acted as an autofilter preventing further action (red light was found experimentally to inhibit the photochemical oxidation of iodoform). In CHCl₃ and CCl₄ solutions the rate of decomposition was slow and solutions developed a colour with a purple tinge, but the

oxidation was complete in one hour. As ether is very volatile, a mixture of ether and benzene has been found to be the most suitable. Moreover, CCl_4 and CHCl_3 being heavier than water settle down preventing the access of oxygen.

Effect of Light of Different Wave Lengths

The effect of light filters on the rate of decomposition of iodoform was also studied using glass filters in presence of various solvents, as shown in Table II. Red filter slowed down the photo-oxidation considerably. This bears the contention of autofilter in the case of ether solution.

A 0.2% solution of iodoform (50 c.c.) in different solvents was exposed to light of different wave lengths under identical conditions, keeping the time of exposure and distance between the lamp and the flask the same.

TABLE II

Exposure = 30 mins. CHI_3 taken = 100 mg.

No. Wave length of filters.	Iodoform found (mg.) in			
	Ether.	Benzene.	CCl_4 .	CHCl_3 .
1. No filter	39.4	84.0	78.1	75.5
2. 640 to 700 $\text{m}\mu$ (red)	17.0	32.8	20.3	38.1
3. 580 to 600 (yellow)	28.9	74.1	63.6	63.0
4. 520 to 580 (green)	28.6	70.8	52.5	59.1
5. 400 to 450 (blue)	35.1	76.8	64.8	65.0

Determination of Ethanol Solution of Iodoform

A solution of iodoform (5-10 c.c.) in ethanol containing not more than 0.1 g. of the substance was pipetted into a 250 c.c. conical flask, and 15 c.c. each of benzene and ether were added. 0.1 N Sodium thiosulphate (10 c.c.) and water (100 c.c.) were also introduced into the flask, which was kept close to the mercury lamp (the distance between the centres of the flask and the lamp was about 5" to 6"). A brownish red colour was observed in the non-aqueous layer due to decomposition of iodoform into free iodine. The flask was shaken from time to time so that the liberated iodine was reduced by sodium thiosulphate solution. This prevented the ether-benzene layer from acquiring a red colour and acting as an autofilter. The flask was shaken once every minute for first 10 minutes, then once every two minutes for next 10 minutes, and later once every five minutes till the non-aqueous layer became colorless. It was then kept under observation for 2 minutes without shaking. The ether-benzene layer during this period developed no colour, indicating complete oxidation. The total time of exposure required for complete photo-oxidation depends upon the following conditions :

1. The amount of iodoform present.
2. The distance of the flask from the mercury vapour lamp.
3. Temperature of the water added.
4. The amount of water added.

Undue long exposures were found to afford higher values for iodoform. Accurate results may be obtained by carrying out experiments with known amounts of iodoform, weights of which are comparable.

After the photo-oxidation was over, the flask was removed from the lamp, and the excess of sodium thiosulphate was titrated with 0.02*N* iodine solution after adding 1 g. of solid potassium iodide and 1 c.c. of starch solution. A blank was also carried out in a similar manner except for the addition of iodoform solution. The difference in the two readings gave the amount of iodine liberated from iodoform.

To avoid any reaction between ether and sodium thiosulphate in light, a dilute solution of sodium thiosulphate was used (reaction is negligible with 0.01*N* thiosulphate). The oxygen present in about 120 c.c. of air enclosed in the flask was found to be enough for the photo-oxidation of 0.1g. of iodoform. (1 c.c. of 0.1 *N* iodine solution \equiv 13.133 mg. of iodoform).

TABLE III
Estimation of iodoform dissolved in ethanol.

Expt. No.	Exposure.	Iodoform.		% Error.
		Present.	Found.	
1.	30 mins.	100.0 mg.	99.88 mg.	-0.12
2.	30	90.0	89.77	-0.30
3.	25	80.0	79.73	-0.30
4.	25	70.0	70.48	+0.60
5.	20	60.0	60.50	+0.80
6.	15	50.0	50.40	+0.80

Estimation of Iodoform suspended in Water.—Suspensions were prepared by weighing iodoform into a 250 c.c. conical flask containing about 100 c.c. of water to which 20 c.c. ether was added. The flask was corked and vigorously shaken till iodoform dissolved completely. About 10 c.c. of benzene and 10 c.c. of 0.1 *N* sodium thiosulphate (by pipette) were added. The flask was exposed to light from the mercury vapour lamp and the amount of iodoform was determined in a manner similar to that already described. A blank was carried out using 100 c.c. of water instead of the suspension.

TABLE IV

Expt. No.	Water.	Exposure.	Iodoform.		% Error.
			Present.	Found.	
1.	50 c.c.	25 mins.	100.0 mg.	100.14 mg.	+0.14
2.	100	30	100.0	99.48	-0.50
3.	100	30	80.0	80.45	+0.60
4.	100	25	70.0	70.48	+0.60

The determination of iodoform by the method described is rapid and simple. It can be used for estimating solutions of organic compounds (such as, acetone) which undergo quantitative iodoform reaction. The method is independent of sunlight as mercury vapour lamp has been used as a substitute. The disadvantage is the expected interference by other iodine-substituted organic compounds as most of them are affected by light.

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