

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY AND PHYSICS OF THE PENNSYLVANIA STATE COLLEGE]

Studies on Acid Iodides. I. The Preparation of Halogen Substituted Aliphatic Acid Iodides with a Note on the Atomic Refractivity of Iodine

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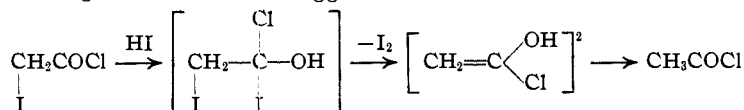
Knowledge of the chemistry of acid iodides is very meager. The difficulties of their preparation, their reactivity and instability doubtless are responsible for the neglect which this group of substances has received. We have been attracted to their study through the hope that their reactivity might make them useful as reagents for achieving unusual chemical transformations.

This paper, the first of a series, deals with the preparation of certain halogen substituted aliphatic acid iodides, and the determination of some of their physical constants.

The most satisfactory method for the preparation of acid iodides is that of Staudinger and Anthes,¹ who prepared acetyl, diphenylacetyl and benzoyl iodides by passing a stream of dry hydrogen iodide into the corresponding acid chloride. This method proved to be very successful for the preparation of chlorinated acid iodides. In this way, monochloro-, dichloro- and trichloroacetyl iodides were easily prepared from the corresponding acid chlorides.

Bromoacetyl chloride was also converted into the corresponding iodide, but attempts to obtain it in a pure form were unsuccessful. It failed to crystallize at -80° , and when warmed to 32° during an attempt at distillation it decomposed with the evolution of heat, forming large amounts of a black crystalline solid, presumably iodine monobromide.

Attempts to prepare iodoacetyl iodide failed completely, as iodine was instantly liberated, even at -10° . This was not surprising, however, as the following set of reactions suggests.



The following table is a summary of the physical constants of these acid iodides.

Iodide	B. p., $^\circ\text{C}$.	Mm.	d_4^{20}	d_{20}^{20}	n_D^{20}	Condition at -80°
CH_3COI	104-106	735	2.0674	2.0710	1.5491	Not crystalline
CH_2ClCOI	36.5	4	2.2607	2.2647	1.5903	Crystalline
CHCl_2COI	54-54.5	15	2.2508	2.2547	1.5754	Not crystalline
CCl_3COI	74-74.2	30	2.2549	2.2589	1.5711	Crystalline
CH_2BrCOI	32° , dec.					
CH_2ICOI	Below -10° , dec.					

(1) Staudinger and Anthes, *Ber.*, **46**, 1417 (1913).

(2) Compare Aschan, *ibid.*, **45**, 1913 (1912).

No determination of the atomic refractivity of iodine in the form of acid iodide has been thus far reported. For this reason the densities and refractive indices of the iodides were determined where possible. The atomic refractivity of iodine as acid iodide has been calculated from the molecular refractivity of acetyl iodide.

Iodide	M _D observed	M _D calculated for CH ₃ CO	Atomic refractivity I ^{-CO-}
CH ₃ COI	26.08	10.35	15.73

Using this value for iodine, the exaltation of the molecular refractivity, EM_D, has been calculated for the chloroacetyl, dichloroacetyl and trichloroacetyl groups as acid iodides. The exaltation was found to be negative in each case.

Iodide	M _D observed	M _D calculated	EM _D
CH ₂ ClCOI	30.52	30.94	-0.42
CHCl ₂ COI	35.08	35.81	-.73
CCl ₃ COI	39.83	40.68	-.85

For purposes of comparison, the atomic refractivities of chlorine, bromine and iodine are shown.

Halogen X	A X ^{-CO-}	B X ^{-CH₂-}	A - B	A + B
Cl	6.336 ³	5.967 ³	0.369	1.0618
Br	9.595 ⁴	8.748 ⁴	0.847	1.0968
I	15.73	13.900 ⁵	1.83	Calcd. 1.133 ⁵ ; found, 1.131

We wish to express our thanks to Dean Frank C. Whitmore for the facilities of this Laboratory, and to the Mallinckrodt Chemical Works for so generously donating the large quantities of iodine necessary for this work. Part of the funds required for this research were privately contributed.

Experimental Part

Acetyl Iodide, CH₃COI.—This substance, b. p. 104–106° (735 mm.), was prepared from purified acetyl chloride by the method of Staudinger and Anthes.¹ These workers, however, submitted no analyses or physical constants other than the boiling point. The iodide did not solidify at -80° (solid carbon dioxide and alcohol). When shaken with mercury, it became colorless.

Anal. (PdI₂) Calcd. for C₂H₃OI: I, 74.69. Found: I, 74.44.

Chloroacetyl Iodide, CH₂ClCOI.—198 grams of chloroacetyl chloride, b. p. 105–106° (740 mm.), cooled to -5°, was treated with 672 g. of dry hydrogen iodide. The resulting reddish liquid was fractionated *in vacuo*.

1st fraction b. p. 30–36.5° (4 mm.)	40 g.	
2d fraction b. p. 36.5° (4 mm.)	245 g.	68% yield
3d fraction b. p. 36.5–37.5° (4 mm.)	25 g.	

(3) Eisenlohr, *Z. physik. Chem.*, **75**, 605 (1911).

(4) Karvonen, *Ann. Acad. Sci. Fennicae*, **A5**, 62 (1914).

(5) Calculated from above two ratios.

The second fraction, b. p. 36.5° (4 mm.) was a heavy, mobile, highly refractive, cherry red liquid of penetrating odor, fuming strongly in moist air. It could be obtained colorless by shaking with mercury, but the red color rapidly returned even if protected from the light at 0°. The iodide sinks in water and, due to its slight solubility, reacts rather slowly to form chloroacetic and hydriodic acids. It dissolves without reaction in the laboratory hydrocarbons, chloroform and carbon tetrachloride. It dissolves in alcohol, reacting instantly with the formation of ethyl chloroacetate. It is soluble in ether and slowly reacts with it, forming ethyl iodide and ethyl chloroacetate. When cooled to -80° the iodide solidified to a mass of colorless leaflets. When shaken with mercury, it became colorless.

Anal. (PdI₂). Calcd. for C₂H₂OClI: I, 62.12. Found: I, 62.39.

Dichloroacetyl Iodide, CHCl₂COI.—Seventy grams of dichloroacetyl chloride, b. p. 106.1–107.1° (739 mm.), was treated with 192 g. of dry hydrogen iodide at -5°. The resulting golden-yellow liquid was distilled *in vacuo*. The distillate, b. p. 50–58° (14 mm.), was then fractionated.

1st fraction b. p. (15 mm.)	50–54	27 g.	
2d fraction b. p. (15 mm.)	54–54.5°	66 g.	58.2% yield
3d fraction b. p. (15 mm.)	54.5–58°	15 g.	

The second fraction, b. p. (15 mm.) 54–54.4°, entirely resembles chloroacetyl iodide in appearance, properties and solubilities. It reacts, however, much more slowly with ethers. It failed to crystallize at -80°. When shaken with mercury, it became colorless.

Anal. (PdI₂). Calcd. for C₂HOCl₂I: I, 53.13. Found: I, 53.60.

Trichloroacetyl Iodide, CCl₃COI.—The preparation of this substance was previously reported by Gal,⁶ who obtained a low yield of doubtless impure material from the reaction of an excess of phosphorus triiodide with trichloroacetic acid. It is easily prepared by the action of hydrogen iodide on trichloroacetyl chloride. 100 g. of trichloroacetyl chloride, b. p. (726 mm.) 116–117°, was treated with 220 g. of dry hydrogen iodide at -5°. The resulting dark red liquid was freed from dissolved iodine by distillation *in vacuo* from mercury, and then fractionated.

1st fraction b. p. (30 mm.)	below 74°	31.2 g.	
2d fraction b. p. (30 mm.)	74–74.2°	107.5 g.	71.5% yield

The second fraction, b. p. (30 mm.) 74–74.2°, resembles in appearance and solubilities the other chlorinated acid iodides, but it is less sensitive to light, and reacts more slowly with water. The most marked difference, however, is its inability to cleave ethers. It solidifies readily at -80° to colorless leaflets. When shaken with mercury, it became colorless.

Anal. (PdI₂). Calcd. for C₂OCl₃I: I, 46.44. Found: I, 46.41.

From the first fraction, after decomposition with water, was obtained a small quantity of an inert liquid with an odor of carbon tetrachloride, b. p. 77–102° (735 mm.), which was not further investigated.

Bromoacetyl Iodide, CH₂BrCOI.—One hundred grams of bromoacetyl chloride, b. p. (737 mm.) 125.0–125.3°, prepared by the method of Hans Meyer⁷ was treated with 244 g. of dry hydrogen iodide at -5°. The liquid rapidly became dark brown. When about one half of the hydrogen iodide had been bubbled in, noticeable amounts of a black crystalline material commenced to precipitate. At the end, the deep reddish

(6) Gal, *Bull. soc. chim.*, [2] **20**, 13 (1873).

(7) Hans Meyer, *Monatsh.*, **22**, 418 (1901).

liquid was decanted from the black precipitate. This crystalline substance gave strong tests for both iodine and bromine, and was possibly a mixture of iodine monobromide and iodine. After unsuccessfully trying to purify the decanted liquid by freezing out crystals of bromoacetyl iodide, an attempt was made to distil it *in vacuo*. When the bath temperature reached 32°, the liquid suddenly decomposed with the evolution of considerable heat, and the formation of large amounts of the black crystalline material mentioned above.

Iodoacetyl Iodide, CH₂ICOI.—Spindler⁸ attempted to prepare this substance by heating chloroacetyl chloride with calcium iodide in a sealed tube. The method of Staudinger and Anthes proved to be equally unsuccessful. Fifty grams of freshly redistilled iodoacetyl chloride, b. p. 31–32° (4 mm.), prepared by the method of Abderhalden and Guggenheim⁹ was placed in a gas wash bottle and cooled to –10°. When dry hydrogen iodide was passed into the liquid, there was an instantaneous precipitation of iodine crystals completely stopping the passage of the gas. Evidently iodoacetyl iodide, if formed, is unstable at –10°.

Summary

1. The method of Staudinger and Anthes for the preparation of acid iodides has been extended to include the preparation of several halogenated aliphatic acid iodides.
2. Chloro-, dichloro- and trichloroacetyl iodides have been prepared by this method, and some of their physical constants and chemical properties have been determined.
3. Bromoacetyl iodide has been prepared, but it was too unstable to permit purification by distillation.
4. Iodoacetyl iodide could not be prepared.
5. The atomic refractivity of iodine as acid iodide, and the exaltation of molecular refractivity for chloro-, dichloro- and trichloroacetyl iodides have been determined.

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(8) Spindler, *Ann.*, **231**, 274 (1885).

(9) Abderhalden and Guggenheim, *Ber.*, **41**, 2853 (1908).