

# THE SOLVENT PROPERTIES OF TRIFLUOROIODOMETHANE\*

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It has been reported<sup>1</sup> that liquid trifluoroiodomethane will dissolve tetramethylphosphonium iodide. As it is unusual for a perhaloalkane to dissolve salt-like compounds a qualitative investigation of the solvent properties of liquid trifluoroiodomethane has been undertaken to determine whether the substance possessed other unusual solvent properties, in particular could it behave as a solvo-system with ionization of the form  $\text{CF}_3\text{I} \rightleftharpoons \text{I}^+ + \text{CF}_3^-$ . Such an ionization had been suggested by Banus, Emeléus, and Haszeldine<sup>2</sup> to explain exchange between iodide ions and trifluoroiodomethane in ethanol. Mason<sup>3</sup> has recently presented evidence based on exchange studies which makes this ionization process extremely unlikely as a mechanism for exchange.

TABLE 1  
SOLUBILITIES IN LIQUID TRIFLUOROIODOMETHANE

<i>T</i>	Soluble	Sparingly Soluble	Insoluble
20°	(CH <sub>3</sub> ) <sub>4</sub> PI; (CH <sub>3</sub> ) <sub>3</sub> CF <sub>3</sub> PI; Ph <sub>3</sub> CH <sub>3</sub> PI; Ph <sub>3</sub> CH <sub>3</sub> AsI; Ph <sub>3</sub> P; Ph <sub>3</sub> As; Ph <sub>3</sub> Sb; NOCl; ICN; ICl <sub>3</sub> ; PCl <sub>5</sub> ; (C <sub>5</sub> H <sub>5</sub> ) <sub>2</sub> Fe	I <sub>2</sub> ; AsI <sub>3</sub> ; SnI <sub>4</sub>	(CH <sub>3</sub> ) <sub>4</sub> NI; PH <sub>4</sub> I; NH <sub>4</sub> BF <sub>4</sub> ; NH <sub>2</sub> OH.HCl; LiCl; KI; CrCl <sub>3</sub> ; PCl <sub>5</sub> ; SbI <sub>3</sub> ; BiCl <sub>3</sub> ; [(CH <sub>3</sub> ) <sub>4</sub> P][HgI <sub>3</sub> ]; [PyH] <sub>2</sub> [HgI <sub>4</sub> ] [(CH <sub>3</sub> ) <sub>4</sub> P][Hg <sub>2</sub> I <sub>5</sub> ]; [PyH] <sub>2</sub> [Hg <sub>3</sub> I <sub>8</sub> ]
-45°		(CH <sub>3</sub> ) <sub>4</sub> PI; ICN	(CH <sub>3</sub> ) <sub>4</sub> NI; [PyH][HgI <sub>3</sub> ]; HgI <sub>2</sub>
-78°		(CH <sub>3</sub> ) <sub>4</sub> PI	

The results of the solubility study are shown in Table 1. Compounds listed as soluble have solubilities *c.* > 1% (w/v) and those as sparingly soluble have solubilities *c.* < 1%. Except for a number of Group VB quaternary 'onium iodides, salt-like compounds are insoluble in liquid trifluoroiodomethane. Compounds which might be expected to undergo solvolysis if ionization of CF<sub>3</sub>I occurred, for example, PCl<sub>5</sub>, SbI<sub>3</sub>, ICN do not appear to react with the solvent and were generally found to be insoluble or sparingly soluble.

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<sup>1</sup> Haszeldine, R. N., and West, B. O., *J. Chem. Soc.*, 1956, 3631.

<sup>2</sup> Banus, J., Emeléus, H. J., and Haszeldine, R. N., *J. Chem. Soc.*, 1951, 60.

<sup>3</sup> Mason, J., *J. Chem. Soc.*, 1960, 4695.

In general it is concluded that the solvent properties of trifluoroiodomethane are as would be expected for a perhaloalkane. However it resembles methyl iodide in its ability to dissolve some quaternary compounds. The chemical similarity between methyl and trifluoromethyl groups has been also observed in exchange reactions involving Group VB alkyl and perfluoroalkyl compounds and related halides.<sup>1,4</sup>

There are two unusual features worthy of mention among the results reported in Table 1.

(a) Tetramethylammonium iodide is insoluble in the liquid whereas tetramethylphosphonium iodide is soluble. This must reflect considerable differences in solvation of the compounds due to some property of the Group V element because the cations appear to have similar sizes from inspection of models.

(b) Tetramethylphosphonium iodide forms a two-layer system in trifluoroiodomethane at room temperature which can be converted to one layer on cooling to  $-3^{\circ}$ . This behaviour is unexpected with solutions of salts and is reminiscent of the behaviour of binary liquid systems. It suggests that the quaternary is behaving more like an undissociated 5-covalent compound in this solvent.

Ferrocene, although dissolving readily in liquid trifluoroiodomethane, does not react with it even at  $130^{\circ}$  in contrast to the behaviour of cobaltocene<sup>5</sup> where substitution of a  $\text{CF}_3$  group and oxidation to the cobalticinium ion have been observed.

### Experimental

Trifluoroiodomethane was prepared by the method of Haszeldine<sup>6</sup> and was purified by trap-to-trap distillation in a vacuum system. Vapour-phase chromatographic analysis failed to show any detectable impurities.

*Solubility Studies.*—The solute (c. 0.01–0.1 g) was sealed in a thick-walled Pyrex tube (c. 40 ml capacity) with sufficient trifluoroiodomethane to yield 2–3 ml of liquid at room temperature. Solubility could be checked by allowing some of the liquid to evaporate on the wall of the tube by tilting and warming. Any residue indicated solution of a solid solute. Low temperature baths were prepared by freezing solvents with appropriate melting points to a slush with liquid air.

*Tetramethylphosphonium Iodide.*—Trifluoroiodomethane (7 g) and tetramethylphosphonium iodide (0.22 g) were sealed in a heavy walled tube. At room temperature ( $20^{\circ}$ ) a two-layer system was obtained the upper layer being colourless and the lower, pale yellow. The colour is believed to be due to traces of iodine in the  $\text{CF}_3\text{I}$  formed by photochemical decomposition giving coloured polyiodide ions. On cooling to  $-3^{\circ}$  the two-layer system formed only one layer and at  $-10^{\circ}$  crystallization of the solute occurred.

*Ferrocene* (0.13 g) was completely soluble in trifluoroiodomethane (4 g) at room temperature. No reaction was observed after 110 hr at  $130^{\circ}$ .

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<sup>4</sup> Haszeldine, R. N., and West, B. O., *J. Chem. Soc.*, 1957, 3880.

<sup>5</sup> Green, M. L. H., Pratt, L., and Wilkinson, G., *J. Chem. Soc.*, 1959, 3753.

<sup>6</sup> Haszeldine, R. N., *J. Chem. Soc.*, 1951, 584.