Comment on "Chlorination and Formation of Organoiodinated Compounds: The Important Role of Ammonia"

SIR: Karpel Vel Leitner et al. (*1*) present an interesting study on how ammonia and chlorine influence the halogenation of organic matter in natural waters in the presence of iodide ion (I^-) and iodine (I_2). These authors show that iodoform is the principal trihalomethane formed when chloramine or organochloramines are present or are in excess. Their work also shows an enhanced effect on iodoform formation in the presence of molecular iodine with excess chloramine but negligible iodoform formation with iodine alone at the same concentration range. Molecular iodine alone at much higher concentrations was shown to produce iodoform.

I wish to report that previous work done on the development of analytical methods for iodine in aqueous solution in the presence of chlorine and chloramines (*2*−*5*) could answer many of the questions raised in the above mentioned study. These analytical studies reveal that the product of most importance from the reaction of iodide ion and iodine with chloramine and organochloramines is hypoiodous acid, HOI:

$$NH_2Cl + I^- + H_2O \rightarrow HOI + NH_3 + Cl^- \quad (1)$$

$$RNCl + I_2 + 2H_2O \rightarrow 2HOI + RNH + Cl^- + H^+ \quad (2)$$

This is most likely the key intermediate reaction step in the production of iodoform. Indeed, hypoiodite ion (OI^-) is the principal reactant employed in the iodoform precipitation method for the identification of certain alcohols and methyl ketones (*6*).

Reactions 1 and 2 offer an explanation for the iodoform production when comparing the reaction products (Tables 3−6) with the breakpoint curves (Figures 1−4). In each case, iodoform is produced only when combined chlorine is present but is formed at very low or nondetectable levels when free chlorine (HOCl) is available. When free chlorine is present, the more common THMs ($CHCl_3$, $CHCl_2Br$, and $CHClBr_2$) begin appearing at elevated levels as would be expected. Some HOI still may be present at this point, but HOCl is a much stronger oxidant and apparently is the predominant player in the chlorinated and brominated THM formation reaction. Also, previous work by Black et al. (*3*) suggests that HOI actually may be destroyed (converted to iodate ion, IO_3^-) in the presence of free chlorine, and Chang (*7*) and this author (*5*) suggest that, over time, HOI is lost through disproportionation to iodate.

Another interesting observation is the enhanced formation of iodoform when molecular iodine is added to iodide ion in the reaction scheme. It is unclear if the authors allowed for the excess iodide ion that is included with the aqueous I_2 solution (at a ratio of 1.9 mg of I^-/mg of I_2). This excess iodide ion also would be oxidized to HOI and enter into the reaction creating the unexplained enhanced formation of iodoform. Or, if the iodine were added on an *equimolar* basis, then reaction 2 offers an explanation for this phenomenon in that for every mol of I_2 added, 2 mol of HOI are produced versus 1 mol of HOI for every mol of iodide ion. Reference *5* provides a thorough explanation of the reaction stoichiometry (for equivalent weights of I^- and I_2) in describing an analytical method for the determination of iodine, iodide, and hypoiodous acid in aqueous solution.

Again, in Figure 6 enhanced production of iodoform is observed when comparing equal concentrations of I^- versus $I^- + I_2$. In the reaction scheme, the specific level of I_2 in combination with I^- is not given, and, again, it is not clear if the authors allowed for the excess I^- associated with the I_2 solution.

The authors also report that molecular iodine alone at low concentration does not cause formation of iodoform but does at higher levels. These reaction schemes were carried out at pH 8. At these levels and at this pH, the majority of I_2 would hydrolyze to HOI (3,7):

$$I_2 + H_2O \leftrightarrow HOI + H^+ + I^-, \quad K_e = 3 \times 10^{-13} (@25\ °C) \quad (3)$$

Apparently, for the lower levels of iodine, some other competitive reaction or iodine demand prevents the formation of HOI, or at pH 8, the small amount of HOI produced by hydrolysis decomposes to iodate before detectable levels of iodoform are produced. For the higher levels of iodine (1 and 2 mg/L) at this pH, Chang (*7*) calculates that as much as 70−80% can exist as HOI. Apparently, these high levels exist long enough to produce significant concentrations of iodoform.

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