1.10 for an average chain length of 2×10^3, and rises to a constant value, or flat maximum, of about 1.20 for an average chain length of 8×10^4.

3. It has been shown qualitatively that the temperature coefficient has a value about 10% higher when "green light" (a $NiSO_4$ filter) is used as the source of activation.

4. An absolute value, of approximately *unity*, for the ratio of the yield per ion pair to the yield per absorbed quantum was obtained using monochromatic light of λ4358 Å. The results of Porter, Bardwell and Lind[1] are discussed, and a correction based upon the work of Allmand and Beesley[4] has been applied.

5. A mechanism of activation, consistent with the results presented here, is outlined.

MINNEAPOLIS, MINNESOTA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF WASHINGTON SQUARE COLLEGE, NEW YORK UNIVERSITY]

THE OXIDATION OF IODIDE ION BY PERSULFATE ION. III. THE IODIMETRIC ESTIMATION OF PERSULFATES

BY CECIL V. KING AND ERIC JETTE

RECEIVED OCTOBER 8, 1929 PUBLISHED FEBRUARY 6, 1930

In the second paper of this series the velocity of the reaction between persulfate and iodide ions in alkaline solutions was reported. The iodine produced disappears almost as fast as formed, producing iodate and iodide (through the intermediate formation of hypoiodite); the liberation of iodine on acidifying was assumed to be quantitative. Some of our experiments suggested that the amount of iodine recovered was slightly low. Consequently the iodimetric estimation of persulfate in neutral and alkaline solutions was carefully compared.

A number of previous investigations have proved that persulfate liberates iodine from potassium iodide with quantitative precision in neutral solution[1] and we have fully confirmed this. The reaction is slow, but can be hastened enormously by inert salts, special catalysts, etc., as shown in the papers mentioned.

Experimental

(1) Liberation of Iodine in Neutral Solution.—We first compared the amount of iodine liberated by potassium permanganate in acid solution with that liberated by an equivalent amount of potassium persulfate in neutral solution. The permanganate was carefully standardized, and the concentrations and conditions used in liberating iodine were well

---

[1] See Müller and Ferber, *Z. anal. Chem.*, **52**, 195 (1913); Müller, *ibid.*, **52**, 299 (1913); Schwicker, *ibid.*, **74**, 433 (1928); Zombory, *ibid.*, **73**, 217 (1928). References to other literature will be found in these papers.

within the limits recommended by Bray and Miller, who have concluded that the permanganate method for standardizing thiosulfate solution is accurate to one part per thousand.[2] Potassium persulfate was recrystallized three times between 50 and 0° and dried over sulfuric acid. Standard solutions were made by weighing out the crystals; 0.008 and 0.04 *M* solutions of persulfate were used. Samples of these solutions, potassium iodide and potassium chloride (to hasten the reaction) were sealed in glass bulbs (to avoid loss of iodine by volatilization) and allowed to stand for one to three hours. Several series of experiments showed agreement to one part per thousand between the two methods. For example, using 0.008908 *M* permanganate (±0.03%) a thiosulfate solution was 0.009841 *M* (±0.04%); using 0.008 *M* persulfate to liberate the iodine, the thiosulfate was 0.009847 *M* (±0.05%). Other trials gave equally good agreement.

(2) **The Reaction in Alkaline Solution.**—Müller and also Schwicker[1] have claimed quantitative results when iodine is liberated by persulfate in alkaline solution which is later acidified just before titration. Most of Müller's titrations show 1 to 2 parts per thousand less iodine than the theoretical, but it is hard to tell from Müller's paper whether this is significant or not. Schwicker reports most of his titrations only to 0.1 cc. and consequently his degree of precision is doubtful. We feel that our experiments are comparable in accuracy to those of Bray and Miller[2] on the use of permanganate in standardizing thiosulfate solutions.

Our very carefully made comparisons show that the iodine liberated in alkaline solution is invariably 2 to 5 parts per thousand lower than the amount which is liberated in neutral solution. The following example from a series of twenty comparisons made will illustrate: neutral solution, 25 cc. of 0.008 *M* persulfate + 5 cc. of *M* KI + 4 g. of KCl required 40.11, 40.14, 40.13, 40.12 cc. of thiosulfate solution; alkaline solution, 25 cc. of 0.008 *M* persulfate + 5 cc. of *M* KI + 10 cc. of *M* NaOH (from sodium), acidified later, required 40.03, 40.04, 40.02, 40.03 cc. of the same thiosulfate solution. In all other experiments, with persulfate 0.008 *M* and 0.04 *M*, the results were similarly low. The difference is quite outside experimental error. We recommend that if the alkaline solution method is used, the results be increased by three parts per thousand to be in agreement with the very accurate neutral solution method.

(3) **Investigation of this Inaccuracy.**—It has apparently been taken for granted that when iodine solution is made alkaline and then acidified, the iodine is quantitatively recovered. However, we have found that this is not the case. In a series of comparisons it was found that the iodine recovered was almost invariably 2 to 5 parts per thousand lower than that in the same sample titrated directly with thiosulfate. For example:

---

[2] Bray and Miller, This Journal, **46**, 2204 (1924).

25 cc. of 0.00880 M iodine (in 0.1 M KI) titrated directly required 20.57, 20.59, 20.55, 20.60 cc. of thiosulfate. The same sample + 5 cc. of 3 N sulfuric acid required 20.60 and 20.58 cc. of thiosulfate. The same sample run into 20 cc. of 3 M NaOH (from sodium), immediately acidified, required 20.52, 20.53 and 20.53 cc. of thiosulfate; acidified after standing for one hour, 20.49 and 20.50 cc. of thiosulfate. About fifty other samples run at widely different times, with different lots of materials, with iodine from 0.005 to 0.02 M and NaOH from 0.5 to 1.5 M, gave results 2 to 5 parts per thousand low in the alkaline solutions.

We are sure that these results are not due to experimental error. All precautions were taken to avoid loss of iodine by volatilization. Sodium hydroxide which had been purified by alcohol was avoided (see Müller, Ref. 1). Comparisons were made under exactly similar conditions. The inaccuracy of the liberation of iodine by persulfate in alkaline solution is undoubtedly due to the same cause as the loss of iodine when the solution is made alkaline and then acid.

The only reasonable explanation seems to be that hypoiodous acid or hypoiodite ion decomposes in some manner such that part of the iodine does not reappear on acidifying. Hypoiodous acid, being more of a base than an acid, exists to an appreciable extent in alkaline solution; it may decompose as follows

$$2HIO \longrightarrow 2I^- + 2H^+ + O_2, \text{ or perhaps } 2IO^- \longrightarrow 2I^- + O_2$$

The yellow color (which does not disappear immediately on making the solution alkaline) and the odor presumably indicate the presence of hypoiodous acid in the alkaline solution.

Summary

1. The amount of iodine liberated from potassium iodide by persulfate in neutral solution is shown to agree within one part per thousand with that liberated by an equivalent amount of permanganate in acid solution. Persulfate is therefore recommended as an oxidimetric standard in iodimetry.

2. When the liberation is carried out in alkaline solution which is acidified just before titration, the results are 2 to 5 parts per thousand low; no way has been found to eliminate this error.

3. When a solution of iodine in potassium iodide is made alkaline, then acidified, 2 to 5 parts per thousand of the iodine are lost. This probably explains conclusion (2).

NEW YORK, N. Y.