Periodate oxidation of saccharides. III.* Comparison of the methods for determining the consumption of sodium periodate and the amount of formic acid formed

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Different methods for determining the oxidizing agent consumption during the periodate oxidation of glucose have been compared. It has been found that the methods requiring alkaline medium are not suitable for the periodate determination. Using these methods, a further periodate consumption may occur during the determination.

On the basis of unexpected differences in the determination of free and bound formic acid formed by periodate oxidation of glycerol and mannitol a possible course of the periodate oxidation of 1,2-diols is discussed.

When investigating the periodate oxidation of glycols and saccharides we have observed several times a disagreement between the oxidizing agent consumption and the determined amount of formic acid formed by oxidation. It has also been noted that the results of determination are dependent on the application of particular methods.

Also other authors, *e.g. Hughes* and *Nevell* [1] found in the periodate oxidation of glucose that after the periodate consumption the amount of formic acid formed during the oxidation was smaller than expected. The authors used three methods for determining the decrease of the periodate ion: *1.* thiosulfate method in acidic medium, *2.* arsenite in alkaline medium according to Fleury—Lange, and *3.* the latter one modified by these authors. They observed that after one-hour oxidation of glucose, the periodate consumption determined by the original Fleury—Lange method was almost 5 moles/mole glucose; however, the result of determination of periodate consumption by thiosulfate in acidic medium reached the value of about 3 moles/mole glucose. The value obtained by the third method was intermediate between the above two.

For the determination of the formic acid formed the authors [1] used the direct titration with sodium hydroxide using phenolphthalein as indicator, which, in agreement with our experiences gave the value close to total formic acid, *i.e.* including the portion bound as formyl derivative. This method proved the formation of 3 moles of formic acid per 1 mole of glucose after one-hour oxidation of glucose; this corresponds to the periodate consumption determined in acidic medium.

Fedoroňko et al. [2, 3] observed during the periodate oxidation of glyceraldehyde that upon 15 minutes' oxidation the periodate consumption determined by the method of Fleury—Lange is theoretical, whereas the formic acid determined alkalimetrically represents only one quarter of the theory.

* For Part II see Ref. [6].

Pratt et al. [4] noted that in the oxidation of sedoheptulosane the theoretical periodate consumption was attained after one hour but the formic acid being formed reached the expected value only after 12 days. The authors have not, however, described the methods of determination they used.

Different methods of the formic acid determination have been compared and the iodometric method of determination both of free formic acid [5] and of formate portion [6] has been worked up. This method provides accurate and reproducible results. The principle of the free formic acid determination lies in the fact that after destroying the excess of periodate with ethylene glycol there are added to the solution potassium iodide and sodium thiosulfate, the excess of which is back-titrated with iodine. The total formic acid determination, including the formate portion, is based on the fact that upon addition of sodium thiosulfate during four-hour standing, hydrolysis of the formate portion of formic acid takes place in the solution by shifting the reaction equilibrium. Hydrolysis thus proceeds in neutral medium which eliminates the errors of alkalimetric method of the formic acid determination. These errors might be due to alkali consumption by aldehyde groups of oxidation products. The application of biamperometric indication eliminates the error of the original iodometric method. In this method starch or amylose were used as indicators, these binding a considerable amount of iodine and thus influencing the accuracy of the formic acid determination.

By means of thus modified method we decided to investigate the periodate oxidation of several model substances, including glucose oxidized in [1], compare the results obtained by different methods, and explain discrepancies in individual determinations. Besides the determination of formic acid, we compared the methods of the periodate determination in acidic and alkaline media with the spectrophotometric method.

Results and discussion

A. Periodate oxidation of glucose

The results of periodate oxidation of glucose are listed in Table 1.

We may conclude from the results obtained that for the determination of periodate concentration the methods requiring alkalinization of the medium before proper determination (methods *2* and *3* in Experimental) are not suitable: in case a product, which is a formyl derivative, has been formed by oxidation, a further consumption of

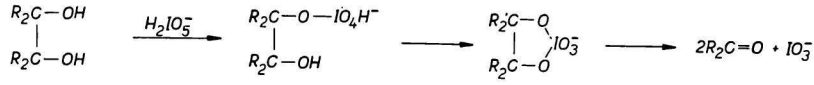
Table 1

Periodate oxidation of D-glucose

Determined moles/mole glucose	Duration of oxidation	
	1 hour	2 hours
Free formic acid	1.93	2.24
Total formic acid	2.97	3.15
Sodium periodate consumption in acidic medium (methods *1* and *4*)	2.98	3.52
Sodium periodate consumption in alkaline medium (methods *2* and *3*)	4.11	5.00

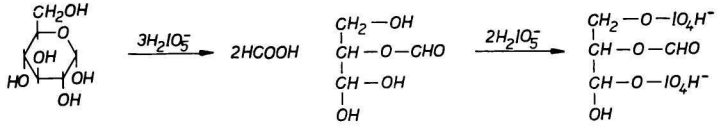
periodate occurs during determination in alkaline medium. The only convenient methods for determining the instant periodate concentration are considered to be the method *1* (*i.e.* in acidic medium) or the method *4* (the spectrophotometric method).

Buist and co-workers [7, 8] proved the following stages of the mechanism of periodate oxidation of 1,2-diols: formation of monoester from periodate ion and hydroxyl group of diol, the ring closure with adjacent hydroxyl group under the formation of a cyclic ester, and the final stage — the ester decomposition into reaction products; the individual stages of reaction are acid-base catalyzed (Scheme 1).



Scheme 1

From this point of view the results of glucose oxidation we obtained may be interpreted as follows. Glucose consumed during the first hour of oxidation (Table 1) 3 moles of periodate mostly for the oxidative cleavage of carbon—carbon bonds C-1—C-2, C-2—C-3, and C-3—C-4 under the formation of two formic acids and a formyl derivative of glyceraldehyde (Scheme 2). The formyl derivatives are relatively stable in slightly acidic medium and only slowly hydrolyze [6]. Thus the formed formyl derivative of glyceraldehyde does not oxidize any more in the solution with the excess of periodate ions and we assume only its esterification.



Scheme 2

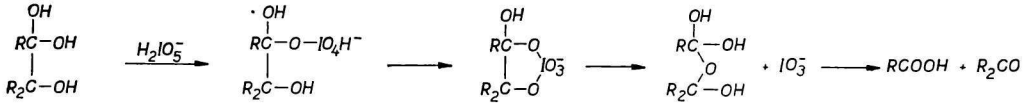
When determining the amount of periodate by means of titration in acidic medium or spectrophotometrically (methods *1* and *4*) the portion of periodate bound as ester is also determined. When using methods *2* and *3* (alkaline medium) for the determination, on addition of alkaline buffer or saturated sodium hydrogen carbonate solution the prompt hydrolysis of formyl derivative takes place. Since the periodate ion is more prone to solvation in alkaline medium [9], the more rapid formation of cyclic ester appears, this being base catalyzed [7] and subsequent decomposition into oxidation products then follows. For this reason, the periodate consumption determined under the given conditions is at the same time of oxidation higher than in the determination by the methods in acidic medium.

B. Periodate oxidation of glycerol and mannitol

We have found in the periodate oxidation of glycerol and mannitol that 2 and 5 moles of periodate respectively, per 1 mole of the corresponding glycol have been consumed after one-hour oxidation; each of the four methods used leads to the theoretical value. The determination of the total formic acid (method *6*) gives also the theoretical value. However, in

the case of glycerol the determined amount of free formic acid is only 82% of its total (method *5*) and even after 120-hour standing it is only 85%; in the case of mannitol it makes 78 and 81%, respectively.

In the course of the periodate oxidation of the substances mentioned above, the formyl derivative, which, in the case of glucose, hinders further oxidation in slightly acidic medium, is not formed. Therefore the oxidation of glycerol and mannitol proceeds continuously and the decrease of periodate determined by different methods is identical. The difference between the determined free and total formic acid not bound as formyl ester remains unexplained. The formation of acylals by the reaction of formic acid with carbonyl groups of the oxidation product or the formation of acylals as intermediate (according to Scheme 3), which is in the given case relatively stable, may be assumed.



Scheme 3

In this reaction mechanism new bond between free oxygen of periodate and carbon atoms of diol would be formed during the oxidation. This may be confirmed by the fact that in the cases when this oxygen is bound in another ester form, oxidation does not take place. This is the case with the periodate oxidation of tridentates [10]. Further, it has been proved on the basis of isotopic reactions with periodate containing isotopes ^{18}O that oxygen in the oxidation products comes from periodate [11].

Experimental

For biamperometric titrations a Multiflex (Lange, Germany) galvanometer was used; sensitivity 4×10^{-9} A/cm, connected with the circuit in the usual manner. The platinum electrodes were supplied with a voltage of 30 mV. Absorbances were measured with an H 700.307 (Hilger, England) spectrophotometer.

Pure glucose and mannitol (Lachema, Czechoslovakia), crystallized from dilute ethanol and glycerol, anal. grade (Strem, Poland) were used. Other chemicals were anal. grade.

Methods

Periodate oxidation

Periodate oxidations of glycerol, D-glucose, and D-mannitol were performed in volumetric flasks in the dark at laboratory temperature. The stock sodium periodate solution (50 mg $NaIO_4$/ml) was added to samples in such an amount so as to obtain 20—50% excess of periodate and its resulting solution of 0.02—0.05 M. After making up to the mark with distilled water, samples were withdrawn in appropriate time intervals to determine the concentrations of sodium periodate and formic acid formed.

Determination of sodium periodate

1. Determination of periodate in acidic medium

1. A sample (content about 1 mg of $NaIO_4$) was pipetted into a beaker with water (about 30 ml), then 0.1 N-H_2SO_4 (5 ml) and 0.4 M-KI (5 ml) were added. On stirring,

0.01 N-$Na_2S_2O_3$ (10 ml) was added and back-titrated with the 0.01 N-I_2 solution by biamperometric indication (consumption $Na_2S_2O_3$ *I*).

II. A sample of solution was pipetted as previously, ethylene glycol (0.5 ml) was added and allowed to stand for 15 minutes. Then 0.1 N-H_2SO_4 (5 ml) and 0.4 M-KI (5 ml) were added and the reaction proceeded in the same way as before (consumption $Na_2S_2O_3$ *II*).

Calculation: 1.07 × (consumption *I* − consumption *II*) = mg $NaIO_4$ in a sample.

2. Determination of periodate in alkaline medium

A sample (content about 1 mg of $NaIO_4$) was pipetted as in the above-mentioned cases, saturated $NaHCO_3$ solution (1 ml), 0.4 M-KI (5 ml), and 0.01 N-$Na_2S_2O_3$ (10 ml) were added. After 15 minutes it was back-titrated with the 0.01 N-I_2 solution by biamperometric indication.

3. Determination of periodate according to Fleury—Lange [12]

To a sample (content about 1 mg of $NaIO_4$) saturated $NaHCO_3$ solution (1 ml), 0.01 N-Na_3AsO_3 (10 ml), and 0.4 M-KI (5 ml) were added. After 15 minutes it was back-titrated with the 0.01 N-I_2 solution by biamperometric indication.

4. Determination of periodate spectrophotometrically [13]

The periodate consumption in samples was determined by measuring the absorbance decrease at 223 nm.

Determination of formic acid

Determination of free formic acid

A sample (content about 1—5 mg of HCOOH) was pipetted into a beaker with water, ethylene glycol (0.5 ml) was added and let stand for 15 minutes. Then 0.4 M-KI (5 ml), 0.01 N-$Na_2S_2O_3$ (10 ml) were added and back-titrated immediately with the 0.01 N-I_2 solution by biamperometric indication.

Determination of total formic acid

The procedure was the same as in the free formic acid determination; however, on adding 0.01 N-$Na_2S_2O_3$ (10 ml) and stirring, the back-titration with the 0.01 N-I_2 was carried out after standing for 4 hours.

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