380. *The Oxidation of Simple Organic Substances by Sodium Metaperiodate in Solutions exposed to Daylight.*

By FRANK S. H. HEAD and G. HUGHES.

Light accelerates the periodate oxidation of a number of simple organic compounds, most of which cannot be regarded as α-glycols (cf. Head, *Nature*, 1950, **165**, 236). The compounds investigated included formic acid and formaldehyde, because the amounts of these produced in periodate oxidations of polysaccharides are sometimes used in calculations of chain length. They, and most of the other compounds investigated, are oxidised ultimately to carbon dioxide and water.

THE rupture of the carbon–carbon single bond in α-glycols and certain related groupings by periodic acid and its salts (Malaprade, *Bull. Soc. chim.*, 1928, [iv], **43**, 683), has been widely applied in the solution of structural problems. It is usually effected at room temperature, and the time of reaction may vary from a few minutes to a day or so. The result is usually almost quantitative, especially when a large excess of oxidant is avoided. However, very few of the products are completely resistant to further oxidation by periodate, and many instances of over-oxidation have been recorded.

Over-oxidation may result from a further glycol cleavage much slower than the main reaction, or from some different type of oxidative process. It can also occur when a side reaction, such as slow hydrolysis, opens the way to further glycol fission; the pH of the reaction mixture may then be an important factor (Head, *J. Text. Inst.*, 1947, **38**, T 389).

Huebner, Ames, and Bubl (*J. Amer. Chem. Soc.*, 1946, **68**, 1621) found that the reactive hydrogen atom in such compounds as malonic acid is rapidly oxidised to hydroxyl by periodate (cf. also Sprinson and Chargaff, *J. Biol. Chem.*, 1946, **164**, 433). The slow oxidation of formaldehyde to formic acid, and of the latter to carbon dioxide (Davidson, *J. Text. Inst.*, 1941, **32**, T 109), may be special examples of Huebner's reaction. Besides being itself responsible for some over-oxidations, this type of reaction, by introducing a new hydroxyl group, sometimes leads to further glycol cleavage.

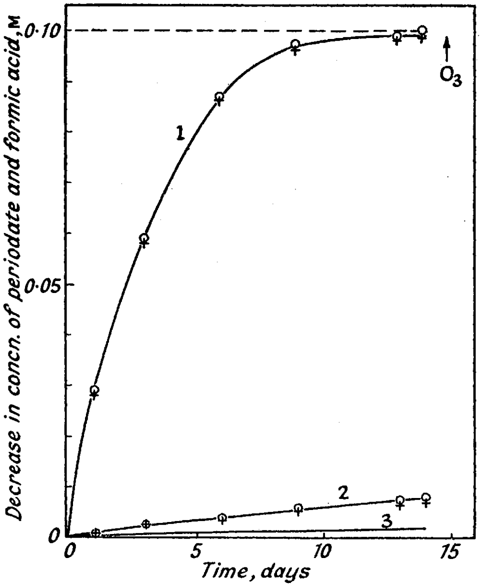
The speed and extent of periodate oxidations are affected, not only by temperature and concentration, but also by the incidence and intensity of daylight as shown by Head (*Nature*, 1950, **165**, 236) for β-methylglucoside, β-methylcellobioside, and cotton cellulose. Rammelsberg (*Pogg. Ann.*, 1868, **134**, 534) reported that pure periodate solutions were unstable and developed a smell of ozone on storage, but Head (*loc. cit.*) found that this occurred only in the light; solutions stored in darkness remained odourless and were stable for many weeks. The instability of the pure solutions in light is due to the autoreduction of periodate to iodate and ozonised oxygen, the reaction being quantitative when the exposure to daylight is sufficiently prolonged. Thus, for reactions in daylight, autoreduction of periodate might be mistaken for over-oxidation of a glycol, if the course of the reaction were followed only by periodate determinations. It has been found that light accelerates the periodate oxidation of a number of simple organic substances, such as formic acid and formaldehyde. In these simple systems the changes in concentration of both oxidant and organic reductants can be followed without difficulty; it is then possible to determine what, if any, part of the change in the concentration of periodate is due to its autoreduction. Particular interest attaches to the behaviour of formic acid and formaldehyde, since attempts are sometimes made to solve constitutional problems, such as the chain length of polysaccharides, by measuring the amounts of these substances produced by periodate oxidation (cf. Halsall, Hirst, and Jones, *J.*, 1947, 1427). The present paper deals, in addition, with methyl and ethyl alcohol, acetaldehyde, and acetic, glycollic, and oxalic acid. Conflicting reports of the behaviour of several of these with periodate under unspecified conditions of illumination occur in the literature.

In the present work pairs of identical reaction mixtures were kept at room temperature under conditions as nearly identical as possible, except that one was exposed to the prevailing daylight and the other kept in darkness. The quantity of periodate taken was usually twice the amount necessary for complete oxidation of the organic substance. A periodate control solution was exposed to light simultaneously. The results are illustrated in Figs. 1—8, which show the changes with time in the compositions of the different reaction mixtures; the term "excess" or "equivalent" used in the legends refers to the proportions of reactants required for oxidation to carbon dioxide and water; the theoretical periodate consumption at this stage is shown by the broken lines in the figures.

Except for acetic acid, which seems to be completely resistant (cf. Fleury and Boisson, *J. Pharm. Chim.*, 1939, **30**, 307), all the substances discussed here are oxidised in light. Some, and possibly all, are oxidised, although much more slowly, in the dark; with methyl and ethyl alcohol no significant reaction occurs within one month. The reactions in the dark are continuous over long periods (cf. Tables 1 and 2, p. 2051), and there is no evidence that they differ, except in speed, from the reactions in the light. For a particular substance the rate is greatly affected by the light intensity and, since this varied both within and between experiments, the results cannot be used to compare the rates of reaction of different substances, or for the kinetic analysis of a particular reaction. Some idea of the variations in light intensity is given by the times required for the concentration of periodate in the control solutions to fall by 1%, which varied from 1 to 13 days.

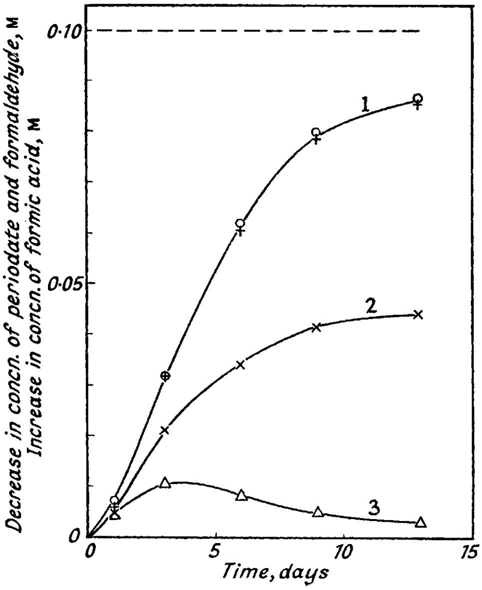
In general, reduction of periodate by the organic substances in daylight was much more rapid than the autoreduction of the corresponding control solution, but the rate differences were not very great with ethyl alcohol and acetaldehyde, which react relatively slowly even in light. With formic acid, formaldehyde, and oxalic acid, it was clear that no measurable autoreduction of periodate occurred concurrently with the main reaction; with the other substances the analytical results were insufficient to enable a conclusion to be drawn. Formic acid, formaldehyde, glycollic acid, methyl alcohol, and oxalic acid can

FIG. 1. *Oxidation of* 0·1M-*formic acid in* 0·2M-*sodium metaperiodate* (100% *excess*).



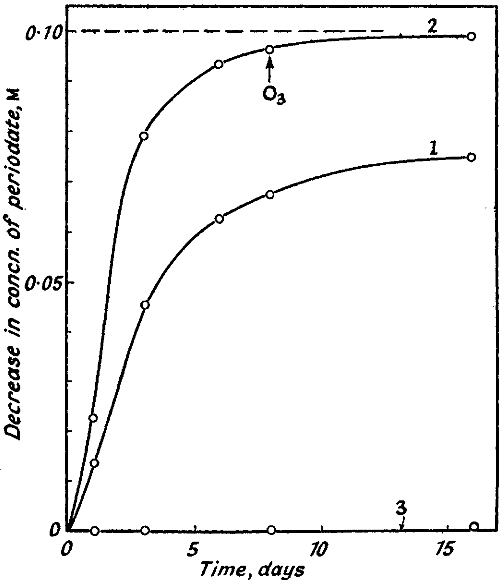
1, *In daylight* : ○, *decrease in periodate* ; +, *decrease in acid.*
2, *In dark* : ○, *decrease in periodate* ; +, *decrease in acid.*
3, *In daylight* : *periodate control.*

FIG. 2. *Oxidation of* 0·05M-*formaldehyde in* 0·2M-*sodium metaperiodate* (100% *excess*) *in daylight.*



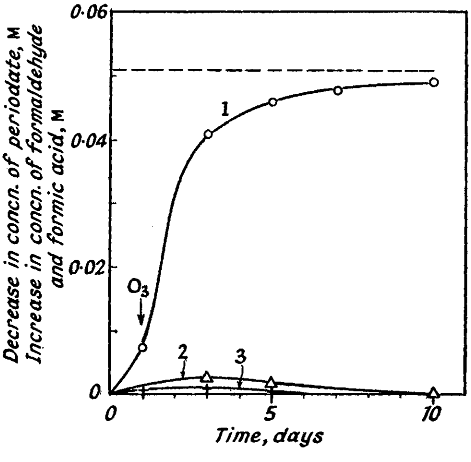
1, *Decrease in periodate* : ○, *obsd.* ; +, *calc.*
2, *Decrease in formaldehyde.*
3, *Increase in acid.*

FIG. 3. *Oxidation of* 0·05M-*formaldehyde in* 0·1M-(*equivalent*) *and* 0·2M- (100% *excess*) *sodium metaperiodate*



1, *In daylight* : 0·1M-*periodate.*
2, *In daylight* : 0·2M-*periodate.*
3, *In dark* : 0·1M- *and* 0·2M-*periodate.*

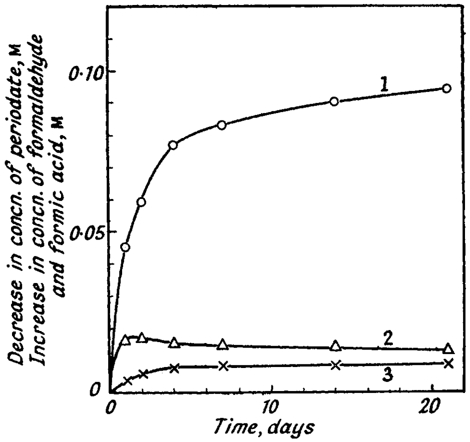
FIG. 4. *Oxidation of* 0·017M-*methyl alcohol in* 0·1M-*sodium metaperiodate* (100% *excess*) *in daylight.*



1, *Decrease in periodate.*
2, *Increase in formaldehyde.*
3, *Increase in acid.*

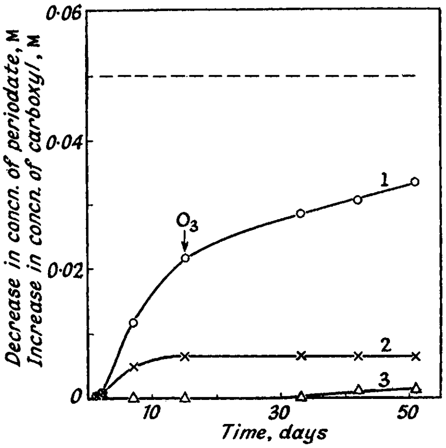
be oxidised completely to carbon dioxide and water in daylight. No smell of ozone was noticed with reaction mixtures containing the first three until oxidation was complete, but ozone was evolved at an earlier stage from mixtures containing the last two. Intermediate products have been detected : *e.g.*, methyl alcohol and glycollic acid give rise to formaldehyde, which, in turn, gives formic acid. With a large excess of periodate in bright sunlight oxidation of formic acid may be complete in as little as one day. It is clearly desirable to carry out Malaprade reactions in the dark whenever the amount of formic acid produced is to be measured.

FIG. 5. *Oxidation of* 0·05M-*methyl alcohol* (50% *excess*) *in* 0·1M-*sodium metaperiodate in daylight.*



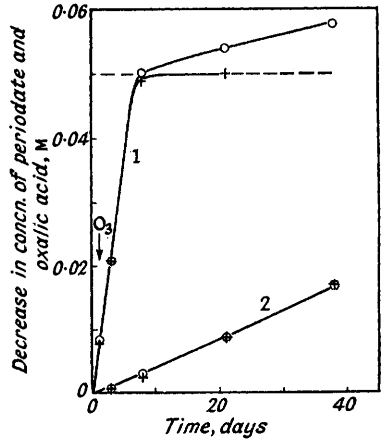
1, *Decrease in periodate.*
2, *Increase in formaldehyde.*
3, *Increase in acid.*

FIG. 6. *Oxidation of* 0·01M-*acetaldehyde in* 0·1M-*sodium metaperiodate* (100% *excess*).



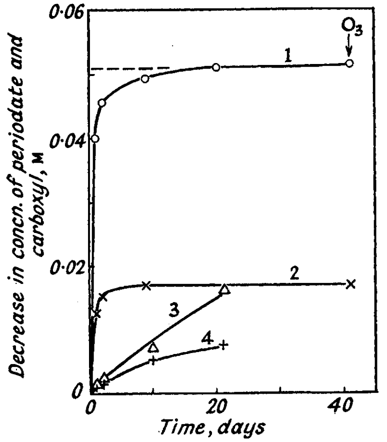
1, *In daylight : decrease in periodate.*
2, *In daylight : increase in acid.*
3, *In dark : decrease in periodate.*

FIG. 7. *Oxidation of* 0·05M-*oxalic acid in* 0·1M-*sodium metaperiodate* (100% *excess*).



1, *In daylight :* ○, *decrease in periodate ;* +, *decrease in acid.*
2, *In dark :* ○, *decrease in periodate ;* +, *decrease in acid.*

FIG. 8. *Oxidation of* 0·017M-*glycollic acid in* 0·1M-*sodium metaperiodate* (100% *excess*).



1, *In daylight : decrease in periodate.*
2, *In daylight : decrease in acid.*
3, *In dark : decrease in periodate.*
4, *In dark : decrease in acid.*

Fleury and Boisson (*Compt. rend.*, 1937, **204**, 1264; *J. Pharm. Chim.*, 1939, **30**, 145) have reported complete oxidation of acetaldehyde by periodic acid at 100°; the intermediate products were methyl alcohol, formaldehyde, and formic (but not acetic) acid.

Complete oxidation has not been achieved under the conditions employed in the present work; the reaction is slow and gives acetic acid (65% yield) which is stable to further oxidation (Fig. 6).

Ethylene glycol reduces periodate almost instantaneously and can be used to remove an excess of the reagent (Halsall, Hirst, and Jones, *loc. cit.*). This reaction is very rapid in the dark also, and it provides a convenient means of preparing standard solutions of formaldehyde in periodate solution. No previous reference to the periodate oxidation of glyoxal has been found, but it, too, reacts very rapidly with periodate, giving formic acid.

In another set of experiments, with formic acid, formaldehyde, methyl alcohol, and oxalic acid, the amount of periodate was only half that required for complete oxidation. Complete reduction of periodate occurred in daylight, and iodine was liberated, as noted in the earlier work with glycosides (Head, *loc. cit.*). Malaprade (*loc. cit.*) noticed this liberation of iodine with an excess of glycol, and it has since attracted the attention of a number of workers who have ascribed it to a variety of specific causes. In our experience, it is always associated with the exhaustion of the available periodate, and, in acid solutions, it gives a good indication of the near approach of this end-point; it is evidence that iodate can act as an effective oxidant (cf. Courtois and Ramet, *Bull. Soc. Chim. biol.*, 1947, **29**, 240).

EXPERIMENTAL

Materials.—Sodium metaperiodate (Hill, *J. Amer. Chem. Soc.*, 1928, **50**, 2678), recrystallised twice from water, was pure according to analysis.

Ethyl alchol, formic, acetic, and oxalic acids were of analytical reagent quality and the methyl alcohol was a carefully fractionated specimen. Acetaldehyde was purified through the ammonia compound. Commercial ethylene glycol was purified by two fractional distillations (the first under reduced pressure). Glycollic acid was recrystallised from a small volume of acetone, powdered, and dried *in vacuo* over phosphoric oxide; it had m. p. 78—79°.

Analytical Methods.—Periodate was determined by Müller and Friedberger's method (*Ber.*, 1902, **35**, 2652). For the determination of acid, the reaction mixture (10 c.c.) was treated with ethylene glycol (5 c.c. of 10% solution), diluted to 55 c.c., and aërated for 15 minutes with air free from carbon dioxide (15—17 l. per hour). Preliminary experiments showed that reduction of periodate was complete, and that carbon dioxide could be removed in this way without measurable loss of formic or acetic acid. The solution was titrated with carbonate-free sodium hydroxide (phenolphthalein).

Formaldehyde was determined by dimedone after removal of periodate and iodate by an adaptation of Reeves's method (*J. Amer. Chem. Soc.*, 1941, **63**, 1476). The reaction mixture (25 c.c.; max. formaldehyde concn. 0·05M), diluted with water (50 c.c.), was treated with N-hydrochloric acid (10—20 c.c.) and an excess of 2·25N-sodium arsenite. Sodium acetate (50 c.c.; 0·4M) was added, followed by sufficient acetic acid to bring the pH to 4·5 (B.D.H. " 4·5 Indicator " was used). The formaldehyde was then precipitated by dimedone (5 c.c. of 10% alcoholic solution); the precipitate was dried to constant weight *in vacuo* over phosphoric oxide. Experiment showed that (*a*) 0·2M-periodate was completely reduced in less than 5 minutes under the above conditions, (*b*) doubling the amount of dimedone taken did not alter the yield from 0·05M-formaldehyde, and (*c*) no precipitate was obtained in the absence of formaldehyde.

Oxidation Procedure.—Suitable reaction mixtures were halved and placed in stoppered Pyrex vessels. One portion was exposed to light and the other kept in an opaque container. Most of the exposures were carried out behind a south-facing window, but often under winter conditions when the light intensity was very low. All experiments were done at room temperature and, in order to maintain equality of temperature, as between the two portions, both were immersed in water in a tank.

Effect of Light on Sodium Metaperiodate Solutions.—0·05M-Sodium metaperiodate, in a closed Pyrex glass tube about 1 cm. in diameter, was exposed to daylight as above. The concentration of periodate in the irradiated solution reached zero after five months. At the end of the exposure the solution gave, with silver nitrate, a precipitate having the characteristic properties of silver iodate, in quantity equivalent to the amount of periodate originally present. The same periodate solution stored for 5 months in a closed glass vessel in the dark at the laboratory temperature showed no change in concentration greater than the probable analytical error. In another experiment, 0·1M- and 0·2M-solutions of sodium metaperiodate contained in gas-burettes of the Bunte type, and acting as their own enclosing liquids, were exposed to daylight as above. A considerable volume of gas collected during a week's exposure to summer sunlight; it was completely absorbed by alkaline pyrogallol, and by alkaline dithionite (hydrosulphite) solution, and consisted chiefly of oxygen with about 1% of ozone. Although ozone is only a minor product of the autoreduction, its intense smell is a very sensitive indication of the decomposition of metaperiodate solutions in light. A 0·03M-solution, prepared and preserved in the dark, remained odourless for many weeks. When exposed to direct sunlight behind glass it developed a faint smell of ozone in 10 minutes, and a strong smell in 2 hours; the same solution exposed only to the diffuse daylight of the laboratory developed a faint smell in 2 hours. All these results were obtained with carefully purified material.

Oxidation of Formic Acid.—The oxidation reaction was followed by determining both formic acid and periodate, and the results of a typical experiment are given in Fig. 1. In daylight, autoreduction of the periodate control (curve 3) is negligible in comparison with the reduction which occurs in the presence of formic acid (curve 1). The amounts of periodate reduced and formic acid destroyed are equivalent for experiments both in the dark and in the light (curve 1 and 2, and Table 1). This, and the absence of any smell of ozone until the reaction is complete, make it unlikely that appreciable autoreduction of periodate occurs when formic acid is present. Oxidation is much more rapid in light than in darkness, but reaction in the dark is nevertheless continuous over long periods of time (Table 1).

TABLE 1. *Oxidation of formic acid* (0·05M) *with sodium metaperiodate* (0·1M).

Light			Dark		
Time	Fall in concn. (M):		Time	Fall in concn. (M):	
(hours)	Periodate	Formic acid	(days)	Periodate	Formic acid
1	0·0068	0·0068	1	0·0012	—
2	0·0112	0·0113	5	0·0021	0·0018
4	0·0170	0·0172	12	0·0030	0·0031
6	0·0237	0·0237	20	0·0044	0·0041
24	0·0336	0·0335	39	0·0078	0·0072
48	0·0472	0·0473	43	0·0084	0·0086

Oxidation of Formaldehyde.—Solutions initially 0·025M in glycol and 0·125M or 0·225M in periodate were prepared from weighed amounts of pure ethylene glycol and periodate. Oxidation to formaldehyde was complete in less than 15 minutes in darkness, and there was no further change in periodate titre for a short time. One mole of glycol consumed 1·002 moles of periodate and gave 2·007 moles of formaldehyde (mean of six experiments). Periodate, formaldehyde, and formic acid were then determined at intervals, and the results of one experiment made in daylight are given in Fig. 2.

Formic acid is an intermediate product of oxidation; its concentration passes through a maximum (curve 3). From the amounts of formic acid and formaldehyde present at any time it is possible to calculate what the fall in periodate concentration should be, provided that there is no autoreduction. The calculated are in good agreement with the observed values (curve 1; cf. also Table 2); if any autoreduction occurs concurrently it must be of very small extent.

Formaldehyde is oxidised much more rapidly in daylight than in darkness. This is shown in Fig. 3, which also compares the reaction rates (simultaneous exposures) in the presence of proportions of periodate equivalent to, and in 100% excess of, that required for complete oxidation; under the latter conditions the consumption of periodate in the illuminated reaction mixture eventually corresponded to complete oxidation of the formaldehyde. Reaction in the dark is slow, but progressive (Table 2).

TABLE 2. *Oxidation of formaldehyde* (0·05M) *with sodium metaperiodate* (0·1M) *in darkness.*

Time (days)	Fall in concn. of formaldehyde (M) (*a*)	Formic acid produced (M) (*b*)	Fall in concn. of periodate (M)	
			Calc. (2*a*–*b*)	Obsd.
7	0·0000	0·0000	0·0000	0·0000
14	0·0002	0·0002	0·0002	0·0001
24	0·0008	0·0008	0·0008	0·0012
50	0·0017	0·0008	0·0026	0·0026

Oxidation of Methyl Alcohol.—In daylight the oxidation leads to formaldehyde (identified as dimedone derivative, m. p. and mixed m. p. 190°), formic acid, and carbon dioxide. With

100% excess of oxidant complete oxidation occurs (Fig. 4), and the amounts of intermediate products detected are small. The smell of ozone develops at an early stage but, in the absence of analyses for either methyl alcohol or carbon dioxide, the extent of any autoreduction of periodate cannot be gauged. With an excess of methyl alcohol over periodate, larger quantities of formaldehyde (up to 33%) and formic acid (up to 17%) are formed (Fig. 5); no ozone is detected, but there is a trace of carbon dioxide. In the dark there is no significant reaction within 20 days.

Oxidation of Acetic Acid.—The titre of a 0·05M-solution of acetic acid in 0·1M-periodate remains unchanged even after 2 months' exposure to direct summer daylight. The periodate titre falls continuously at a rate similar to that of the periodate control, and there is a strong smell of ozone from the outset. It seems clear that the fall in periodate titre is due to autoreduction, and that, apart from the possibility of per-acid formation, acetic acid is completely resistant to oxidation.

Oxidation of Acetaldehyde.—Oxidation proceeds slowly in the light, but ozone is not noticed with solutions which smell strongly of the aldehyde. With a very dilute solution (Fig. 6) it is noticed after 15 days; after 42 days the aldehyde smell can no longer be detected. The quantity of acid formed reaches a maximum after about 15 days and remains constant for a long time. This suggests that the product is acetic rather than formic acid, which is confirmed by potentiometric titration (glass electrode); the p*K* was 4·70, the value for acetic acid being 4·76 and for formic acid 3·75. The yield of acetic acid was 65%. It remains possible that some formic acid may arise in the early stages of the oxidation, but it is doubtful whether acetaldehyde can be oxidised completely to carbon dioxide and water in daylight. Oxidation in the dark is extremely slow.

Oxidation of Ethyl Alcohol.—In darkness, there is no measurable reaction within 35 days. In daylight slow reduction of periodate occurs. Acid is formed, and acetaldehyde can be detected both by its smell and as the dimedone compound (yield *ca.* 16% after 35 days), which, however, appears to be impure; it had m. p. 134—136°, but, mixed with authentic material (m. p. 141°), 134—139°. Despite the slowness of the reaction, there is no smell of ozone.

Oxidation of Oxalic Acid.—Oxidation occurs at an appreciable rate in the dark, and is relatively rapid in daylight. Fig. 7 shows that there is good agreement between the amounts of oxalic acid and periodate consumed until oxidation of the acid is complete (*ca.* 10 days). The subsequent divergence of the two curves is due to autoreduction of periodate. Although the measurements provide no evidence of autoreduction during the oxidation of the acid, there was, nevertheless, a smell of ozone from the first day.

Oxidation of Glycollic Acid.—Oxidation is relatively rapid even in the dark, and complete oxidation occurs within about 2 days in bright sunlight, or 10 days in diffuse light (Fig. 8). At this stage about 3 moles of periodate have been reduced per mole of glycollic acid, and the acidity has completely disappeared. Ozone is detected only at the end of the oxidation. It is probable that formic acid is produced at some stage, and the values for fall in acidity must be regarded as net decreases. Formaldehyde was detected (dimedone compound, m. p. and mixed m. p. 190°) at certain stages in both the light and dark reactions.

Oxidation of Glyoxal.—Redistilled monomeric glyoxal (Harries and Temme, *Ber.*, 1907, **40**, 165) was dissolved in dry benzene and the solution shaken with water. The aqueous layer was freed from benzene by aëration and filtered, and its concentration determined by Friedemann's hydrogen peroxide method (*J. Biol. Chem.*, 1927, **73**, 331) and by iodometry (cf. Head, *J. Text. Inst.*, 1947, **38**, T 389). With a solution which was 0·020M in glyoxal and 0·027M in periodate, the consumption of oxidant (determined by Fleury and Lange's method, *J. Pharm. Chim.*, 1933, **17**, 107) reached 0·99 mole per mole of glyoxal after 8 minutes and remained constant during several hours. (This part of the work was done before the discovery of the light effect.) The corresponding figures for formic acid produced were: 1·84 (5 mins.); 1·94 (15 mins.); 1·99 (30 mins.); 2·01 (1, 3, and 6 hours). Hughes and Nevell (*Trans. Faraday Soc.*, 1948, **44**, 941) reported a similarly delayed appearance of formic acid during the oxidation of glucose by periodate.

BRITISH COTTON INDUSTRY RESEARCH ASSOCIATION,
SHIRLEY INSTITUTE, DIDSBURY, MANCHESTER.

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