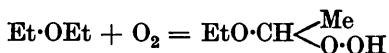


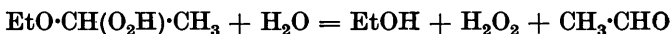
CIV.—*Diethyl Ether. Part I. . The Products of its Autoxidation.*

By HAROLD KING.

FROM the observations of numerous workers it has long been established that diethyl ether may undergo change on storage with production of acetaldehyde and peroxides. It is only within the last few years, however, that any advance has been made in the elucidation of the constitution of the peroxides formed. In 1922 Clover (*J. Amer. Chem. Soc.*, **44**, 1107) published the results of a close study of the autoxidation of ether and drew the conclusion that the peroxide in ether is formed by addition of a molecule of oxygen to a molecule of ether :

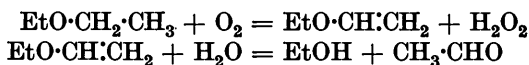


Under the action of acidified water this product undergoes irreversible hydrolysis with production of acetaldehyde, ethyl alcohol, and hydrogen peroxide :

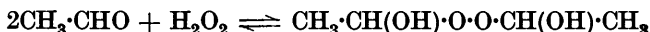


In 1923, however, a different view was advanced by Wieland and Wingler (*Annalen*, **431**, 301), who suggested that the first action of oxygen was a dehydrogenation of diethyl ether with production of ethyl vinyl ether and hydrogen peroxide. The ethyl vinyl ether

then underwent hydrolysis with formation of ethyl alcohol and acetaldehyde :



The acetaldehyde and hydrogen peroxide thus formed combined with production of diacetaldehyde hydrogen peroxide (di- $\alpha$ -hydroxyethyl peroxide),



the equilibrium being in favour of the right-hand side. Such a combination of aldehydes and hydrogen peroxide had been established in the analogous cases of benzaldehyde, formaldehyde, and hydrogen peroxide by Nef (*Annalen*, 1897, **298**, 292) and of chloral and hydrogen peroxide by Baeyer and Villiger (*Ber.*, 1900, **33**, 2484). Wieland and Wingler supported their view by a comparison of synthetic di- $\alpha$ -hydroxyethyl peroxide with the peroxide left on evaporation of rich peroxidic ethers.

The two opposing views bear this resemblance, that the simple units concerned in the changes are the same and in the same proportions. They differ in that, in the one case, the substance responsible for the peroxide reactions in deteriorated ethers is hydrolysed irreversibly to an equimolecular mixture of acetaldehyde and hydrogen peroxide (Clover), whereas, in the other, agents of hydrolysis would produce two molecules of acetaldehyde to one molecule of hydrogen peroxide (Wieland). Wieland and Wingler's proposition of di- $\alpha$ -hydroxyethyl peroxide as the peroxide in ether ignores the fate of the other molecule of uncombined hydrogen peroxide produced in their scheme of autoxidation of the ether molecule. The experimental results of these two groups of workers do not allow a final decision to be made as to which view is correct, and it is evident that new experimental modes of attack are necessary.

The methods which have been proposed for the estimation of peroxides in ether usually depend on the liberation of iodine from potassium iodide, and they require some time for the completion of the reaction. A rapid method giving reproducible results has now been devised depending on the liberation of hydrogen peroxide in acid solution from the peroxides and its titration by permanganate in the presence of manganese salts. It was controlled on acetaldehyde-hydrogen peroxide mixtures in ether. Using this mode of titration it is not uncommon to find Winchester-quart bottles of old ether which contain peroxides equivalent to from 3 to 6 grams of hydrogen peroxide per litre. When such ether is distilled through a column, the peroxides remain behind quantitatively, so

that accumulation of dangerous amounts of peroxides, leading to the explosions so frequently recorded in the literature, is not surprising, especially where the evaporation of large volumes of deteriorated ether is carried out.

The permanganate titration gives a measure of hydrogen peroxide either free or in labile combination. It is directly applicable to the ethereal solution, to the residue obtained on removal of the ether in a vacuum, or to the parallel products from acetaldehyde and hydrogen peroxide mixtures. It fails, however, with *s*-dihydroxydimethyl peroxide, a crystalline substance soluble in water and temporarily stable to acidified permanganate. The estimation of acetaldehyde may be effected by an application of Ripper's method (*Monatsh.*, 1900, **21**, 1079). Using these two methods, with adequate control experiments at every stage, it has been possible to throw new light on the constitution of the main peroxide in ether and to adduce evidence pointing to the existence of a second peroxide of greater stability.

A known volume of ether containing peroxide is evaporated rapidly in a vacuum desiccator over sulphuric acid. The syrupy residue is kept *in situ* for 15 to 30 minutes after all the ether has been removed; it is then dissolved in water to a known volume, and an aliquot part acidified and titrated with permanganate. The remainder is transferred to a flask, treated with acid, and distilled into standard sodium hydrogen sulphite solution. The residue in the distillation flask is titrated with permanganate, and a back titration made of the sulphite in the absorption flasks with iodine. Control experiments on pure aqueous acetaldehyde solutions of concentrations comparable with those which arise in experiments with ether show agreement to within 1 or 2%. Similar experiments on ethereal solutions of acetaldehyde and hydrogen peroxide made up in the molecular ratio 2 : 1 indicated perfect agreement between the two permanganate titration figures, namely, before and after distillation, showing that there is no destruction of hydrogen peroxide under the particular experimental conditions used. Moreover, the acetaldehyde : hydrogen peroxide ratio in duplicate experiments was 1.83 : 1 and 1.91 : 1 instead of 2 : 1. If to this synthetic di- $\alpha$ -hydroxyethyl peroxide in ether, excess of acetaldehyde was added and the solution kept for some hours over dry sodium sulphate, a redetermination of the ratio of acetaldehyde to hydrogen peroxide gave 2.2 : 1 and 2.1 : 1. When, however, a natural peroxide ether (*i.e.*, diethyl ether containing peroxide produced by autoxidation) was submitted to the same process, the aldehyde estimations proceeded normally but there was always a discrepancy between the two permanganate titration figures, the one obtained

on the distillation residue being larger by about 10%. This behaviour is also met with when the ethereal solutions are submitted to a preliminary purification for removal of acetic acid and formic acid, which are always found to a small extent in the products of the autoxidation of ether. It is also independent of the sample of ether used. The results suggest the presence in peroxidised ether of a peroxide more stable than the simple additive type of compound in which acetaldehyde and hydrogen peroxide are concerned, one in which the hydrogen peroxide is revealed only after boiling with dilute sulphuric acid. The presence of *s*-dihydroxydimethyl peroxide would in many ways fit the observations, but no evidence could be found for the presence of formaldehyde in the distillate.

The results of the determination of the acetaldehyde : hydrogen peroxide ratio on natural peroxidic ethers, whether treated with dilute alkali to remove acids or not, indicate a much lower ratio of acetaldehyde to hydrogen peroxide than 2 : 1, and this is confirmed by allowing such ethers to react with excess of acetaldehyde; the ratio then approximates to the 2 : 1 ratio. The summary of the results for a group of ethers is shown in the following table.

Peroxidic ether.	Aldehyde : hydrogen peroxide.		
Synthetic (2 : 1) .....	1.91 : 1	1.83 : 1	1.82 : 1
Synthetic + acetaldehyde .....	2.2 : 1	2.1 : 1	
Natural B (untreated) .....	1.24 : 1	1.32 : 1	1.30 : 1
Natural B + acetaldehyde .....	2.1 : 1	2.3 : 1	
Natural X (untreated) .....	1.13 : 1	1.13 : 1	
Natural X + acetaldehyde .....	2.21 : 1		
Natural A (treated) .....	1.16 : 1	1.13 : 1	
Natural C (treated) .....	1.28 : 1		

From these results it is evident that the peroxides which develop in natural ethers, whether submitted to a preliminary treatment with weak alkali to remove acids or not, contain acetaldehyde and hydrogen peroxide approximately in the ratio 1 : 1 rather than 2 : 1, the mean of the above figures being actually 1.2 : 1. Now this ratio is that which would be produced by the breakdown of Clover's peroxide or by Wieland and Winkler's suggested mechanism for the autoxidation of the ether molecule. The observation, however, that the natural peroxidic ethers can fix more acetaldehyde when it is added to their solutions, and fix it, moreover, in the proportion 2 : 1, is quite incompatible with Clover's formulation of the constitution of the peroxide. It is, however, consistent with Wieland and Winkler's view that the peroxide in ether is essentially a combination of acetaldehyde and hydrogen peroxide, and it is also consistent with their view that these constituents are produced during the autoxidation of ether. Although it is true that the ethers examined above had been kept for several years for the accumu-

lation of peroxides, so that changes in the acetaldehyde : hydrogen peroxide ratio might have taken place, the available evidence points in the other direction. The formation of acetic acid, presumably by interaction between acetaldehyde and hydrogen peroxide in molecular proportion, proceeds to a small extent in comparison with the amount of acetaldehyde and hydrogen peroxide present, and would, moreover, leave the acetaldehyde : hydrogen peroxide ratio unchanged. The catalytic decomposition of hydrogen peroxide, however, would be a much more serious factor ; it might incidentally account for the deficiency of hydrogen peroxide in the ratio of acetaldehyde to hydrogen peroxide found (1.2 : 1), but evidence will be forthcoming in subsequent Parts of this investigation to show that acetaldehyde has a stabilising action on hydrogen peroxide in ether.

Since it is now established that in the autoxidation of ether, acetaldehyde and hydrogen peroxide accumulate approximately in the ratio 1 : 1, the question arises whether one is dealing with a monoacetaldehyde hydrogen peroxide, or with a mixture in equimolecular proportion of hydrogen peroxide and di- $\alpha$ -hydroxyethyl peroxide. Without a close study of the equilibrium which exists in ethereal solution between acetaldehyde and hydrogen peroxide it is not possible to give an exact solution of this problem, but that the former view is probably correct follows from experiments on the partition coefficients of these peroxides between water and ether. In dilute solution, for example, 1%, Clover found that hydrogen peroxide was about 16 times as soluble in water as in ether, in substantial agreement with the results of Ossipoff and Popoff (*J. Russ. Phys. Chem. Soc.*, 1903, **35**, 637), and in more concentrated solution, 5%, Walton and Lewis (*J. Amer. Chem. Soc.*, 1916, **38**, 633) found a coefficient of 9. For the natural peroxide in ether Clover found coefficients of 1.7 and 2.0 in favour of ether, and the present author, using synthetic di- $\alpha$ -hydroxyethyl peroxide containing a slight excess of acetaldehyde, finds a coefficient of 1.5 in favour of ether. With these data available, a natural, untreated peroxidic ether was rapidly washed three times with one-tenth of its volume of water, the aqueous extracts were combined, and the ratio of acetaldehyde to hydrogen peroxide was determined on the extract. The value found was 1.4 : 1, a value which is incompatible with the view that the peroxide is an equimolecular mixture of hydrogen peroxide and di- $\alpha$ -hydroxyethyl peroxide, but consistent with the formulation of the peroxide as mainly monoacetaldehyde hydrogen peroxide,  $\text{CH}_3\cdot\text{CH}(\text{OH})\cdot\text{O}\cdot\text{OH}$ .

Whilst it appears that Wieland and Wingler's view of the production of acetaldehyde and hydrogen peroxide in equimolecular

proportion during the autoxidation of ether is substantially correct, their formulation of these components as uniting with almost exclusive formation of di- $\alpha$ -hydroxyethyl peroxide, leaving the fate of the remaining molecule of hydrogen peroxide undecided, is, on the evidence presented here, untenable.

Woker (*Ber.*, 1914, 47, 1024) found that a mixture of formaldehyde and hydrogen peroxide in aqueous solution had the property of giving a blue colour with benzidine without the use of peroxidase, a property not exhibited by the constituents separately. Wieland and Winkler showed, however, that the property is lost with time or on warming, and suggested that the blue colour was produced by the intermediate monoformaldehyde hydrogen peroxide and not by the final product, *s*-dihydroxydimethyl peroxide. The same has now been found to apply to acetaldehyde and hydrogen peroxide mixtures, the blue benzidine reaction of mixtures of acetaldehyde and hydrogen peroxide in the ratio 2 : 1 being initially intensely positive, but disappearing with time. The peroxide, however, from natural ether, in all the examples examined, gave a positive reaction.

To summarise, the main peroxidic constituent of deteriorated ether is monoacetaldehyde hydrogen peroxide, but there are indications of a second peroxide of more stable type.

#### EXPERIMENTAL.

*Titration of Peroxides in Ether.*—A simple and rapid method for determining the peroxide content of deteriorated ethers is the following : 5 or 10 c.c. of the ether are added to 50 c.c. of approximately *N*-sulphuric acid in a 200 c.c. bottle, followed by a few crystals of manganese sulphate. *N*/10-Potassium permanganate is then run in slowly with rotation of the contents of the bottle to ensure extraction of the peroxides by the aqueous layer. The end-point is taken when the pink colour produced by two drops of permanganate has not completely faded in 10 seconds. This gives a measure of free hydrogen peroxide or that set free from labile compounds by the acid solution. The consumption of permanganate is independent of the presence of acetaldehyde or formic acid, both of which occur in peroxide-rich ethers.

The validity of the method is shown as follows : Perhydrol (3 c.c.) was shaken once with 50 c.c. of dry ether, and the ethereal solution of hydrogen peroxide dried over sodium sulphate. The hydrogen peroxide content was determined on 5 c.c., which required 32.3 and 32.26 c.c. of *N*/10-permanganate in duplicate experiments. To the residual volume of ether (40 c.c.), acetaldehyde (slightly more than 2 mols.) was added (2 c.c.). On titration of 5 c.c. as

before, 30.93 c.c. of *N*/10-permanganate were required or 32.5 c.c. when a correction is applied for the increase of volume on addition of the acetaldehyde. When dihydroxydimethyl peroxide is added to *N*-sulphuric acid there is no comparable immediate consumption of permanganate.

As examples of the potential hydrogen peroxide content of deteriorated ethers the following values may be given. Four Winchester-quart bottles of methylated ether of different origin, left untouched on shelves exposed to daylight for a period not less than 4 years, gave potential hydrogen peroxide contents of A, 5.6 g.; B, 3.8 g.; C, 3.0 g.; and X, 2.8 g. per litre. These ethers had not become markedly diminished in volume by evaporation. Another much smaller bottle of ether, in which some concentration had been effected by evaporation, showed a content of 10 g. of hydrogen peroxide per litre.

*Effect of Distillation on the Peroxide Content of Ether.*—An ether (985 c.c.) which contained an available hydrogen peroxide content of 1.24 g. per litre was slowly distilled through an 8-bulb pear column. After the removal of 840 c.c. the residue, 145 c.c., contained available hydrogen peroxide equivalent to 8.36 g. per litre (calc., 8.42). There is thus no loss of peroxide content on distillation through an efficient column. This is also confirmed by sensitive qualitative tests for peroxides in the distillate. If, however, ether containing peroxides be distilled without a column, some peroxides pass over with the ether.

*Detection of Hydrogen Peroxide in Peroxide-rich Ethers.*—Several workers have recommended the chromic acid test for the detection of free hydrogen peroxide in ether. If no organic peroxides are present, one part of hydrogen peroxide in 400,000 parts of ether may be detected by the technique described below. In the presence of acetaldehyde the test is untrustworthy. The compounds formed between acetaldehyde and hydrogen peroxide are so labile to acids that it is extremely doubtful whether the hydrogen peroxide detected is initially free or not. Certain substances present in peroxidic ethers appear to inhibit this reaction. For instance, a natural ether rich in peroxides and of known peroxide content gave a very faint blue colour, but an ether containing the same amount of hydrogen peroxide with one or two mols. of added acetaldehyde and dried over sodium sulphate always gave a much more intense reaction.

*Detection of Hydrogen Peroxide in Ether.*—One part of hydrogen peroxide in 400,000 parts of ether may be recognised by adding 9 c.c. of the ether to 1 c.c. of water to which has been added 1 drop of 2*N*-sulphuric acid and 1 drop 0.5*N*-potassium dichromate solution

and shaking the mixture in a stoppered cylinder for 30 seconds. On decanting the ethereal layer into a narrow test-tube (0.9 cm. internal diameter) and viewing the contents vertically, a faint blue colour is just recognisable and is unmistakable when compared with a control tube of pure ether. The same dilution of peroxide may be detected in 2 c.c. of ether by Jorissen's vanadic acid reagent (Baskerville and Hamor, *J. Ind. Eng. Chem.*, 1911, 3, 301). For this purpose 0.5 c.c. of the reagent is diluted with 1.5 c.c. of water and shaken for 30 seconds in a stoppered tube with 2 c.c. of the ether under examination. A brownish-orange colour is just detectable in comparison with a control.

*Synthetic Di- $\alpha$ -hydroxyethyl Peroxide in Ether.*—Merck's perhydrol (3 c.c.) was extracted twice, each time with 50 c.c. of sodium-treated ether, and the extracts were combined and dried by addition of freshly ignited sodium sulphate. The ethereal solution (91 c.c.) was decanted into a measuring cylinder, 1 c.c. removed, and its hydrogen peroxide content determined by permanganate (Found: 1 c.c. of ether equivalent to 4.64 c.c. of *N*/10-permanganate). To the solution 2 mols. of acetaldehyde (2.3 c.c.) were added, followed by anhydrous sodium sulphate. When the ethereal solution was rapidly evaporated in a vacuum, di- $\alpha$ -hydroxyethyl peroxide was left as a clear syrup. This substance has a faint odour of acetaldehyde, but the main odour resembles that of the residue obtained on evaporation of deteriorated ethers without the pungent odour due to formic acid. Attempts to crystallise the peroxide failed, but small quantities could be distilled along a test-tube by careful application of heat.

*Determination of the Ratio Acetaldehyde : Hydrogen Peroxide.*—Of the above ethereal solution, 10 c.c. were transferred to a 25 c.c. standard flask and the ether was removed by evaporation at room temperature for 45 minutes in a desiccator containing sulphuric acid and evacuated by a good water-pump through a calcium chloride guard-tube. The ether had usually evaporated in 30 minutes and drying was continued for about 15 minutes. The clear syrupy residue was dissolved in water and made up to 25 c.c. with water, and an aliquot portion (10 c.c.) transferred to a small flask fitted with a dropping-funnel and delivery tube containing a spray trap. The delivery tube was attached to a water-condenser which led into three successive flasks containing 25 c.c., 20 c.c. of standard sodium hydrogen sulphite solution and 15 c.c. of saturated sodium hydrogen carbonate solution. Through the dropping-funnel 25 c.c. of 2*N*-sulphuric acid and 15 c.c. of water were slowly run in and when all was added the contents of the flask were gently boiled for 20 minutes. The acetaldehyde was fixed by the sodium hydrogen sulphite and back titration with standard iodine gave



the amount of uncombined sulphite. The sodium hydrogen carbonate solution served as a trap for volatile sulphur dioxide, which usually amounted to a fraction of a c.c. of *N*/10-iodine solution. After the distillation was complete the residue in the distillation flask was cooled, diluted slightly, and titrated with standard permanganate. This gave the hydrogen peroxide content and in the case of synthetic acetaldehyde hydrogen peroxides should agree with the figure obtained by direct titration of the original 15 c.c. left after removal of the aliquot portion for distillation.

The results of such an experiment are given below. Total back titre of sodium hydrogen sulphite and sodium hydrogen carbonate, 58.37 c.c. of *N*/10-iodine; original titre of sulphite, 91.99 c.c., whence sulphite fixed by acetaldehyde is 33.62 c.c. of *N*/10-iodine. Direct titration of 15 c.c. of the original peroxide solution, 27.64 c.c. of *N*/10-permanganate, whence for 10 c.c., 18.43 c.c. of *N*/10-permanganate. Titration of distillation residue, 18.54 c.c. permanganate, in good agreement with the preceding value. Hence, molecules of acetaldehyde : molecules of hydrogen peroxide = 33.62 : 18.43 or 1.82. Repetition of the process gave values 1.83 and 1.91, indicating that about 93% of two molecules of acetaldehyde remain attached to one molecule of hydrogen peroxide after evaporation of the ethereal solution in the manner described above.

The quantitative estimation of acetaldehyde by this method was controlled by distillation in the same apparatus of a standard solution of comparable concentration, 0.322 g. per 100 c.c., and recovery of 0.325 g. per 100 c.c.

*Effect of Excess of Acetaldehyde on the Aldehyde : Hydrogen Peroxide Ratio.*—To about 25 c.c. of the above ethereal solution a further 1 c.c. of acetaldehyde was added and the solution kept over sodium sulphate. Ten c.c. were then removed and analysed in precisely the same way as described above, evaporation of the ethereal solution being prolonged to 1 hour to effect removal of uncombined acetaldehyde. The ratios obtained in duplicate experiments were aldehyde : hydrogen peroxide = 2.2 and 2.1.

*Ratio of Aldehyde to Hydrogen Peroxide in the Peroxides of Untreated Ether.*—Two Winchester quarts of ether of different origin had been left exposed to daylight for several years. The aldehyde : peroxide ratio was determined as described above, but the figures require detailed consideration. For instance, 25 c.c. of an old methylated ether B were evaporated in a 50 c.c. standard flask for 90 minutes in a vacuum, removal of the ether taking 75 minutes. The volume was made up to 50 c.c. with water, 25 c.c. were transferred to the distillation apparatus, and the aldehyde was distilled after the addition of 25 c.c. of 2*N*-sulphuric acid. The sulphite

consumed by aldehydes was equivalent to 41.3 c.c. of *N*/10-iodine. On direct titration of 25 c.c. of the original solution, the peroxide was equivalent to 28.53 c.c. of *N*/10-permanganate and titration of the distillation residue showed peroxide equivalent to 31.68 c.c. of *N*/10-permanganate. There is thus a discrepancy of about 10% in the two permanganate titration figures and it is always found when the residues from natural peroxidic ethers are examined. When the flask giving the low titre was kept for 30 minutes, it straightway consumed a further 0.5 c.c. of *N*/10-permanganate, indicating the generation of hydrogen peroxide from a more stable complex than di- $\alpha$ -hydroxyethyl peroxide. The behaviour can be imitated by adding *s*-dihydroxydimethyl peroxide to *N*-sulphuric acid and then adding permanganate. No reaction takes place, but with lapse of time hydrogen peroxide is slowly generated and can be titrated. If the mixture is kept for many hours, a much larger consumption of permanganate will take place immediately. The figure given by the titration of the distillation residue thus gives a more correct value for the peroxide content than the direct titration. Hence molecules of acetaldehyde : hydrogen peroxide =  $41.3 : 31.68 = 1.3$ . In duplicate experiments, the values found were 1.24 and 1.32; mean 1.29. This indicates that only 64% of two molecules of aldehyde are present to one of hydrogen peroxide.

Another methylated ether, X, gave the molecular ratio acetaldehyde : hydrogen peroxide, 1.13 : 1 and 1.13 : 1.

An attempt to detect formaldehyde in the distillate was made by evaporating the ether from 20 c.c. of ether B and distilling the residue from *N*-sulphuric acid into a few c.c. of water. The distillate gave a strong aldehyde reaction with Schiff's reagent, but failed to respond to Denigès' sensitive reaction (*Compt. rend.*, 1910, 150, 529) for formaldehyde in the presence of acetaldehyde. A mixture of acetaldehyde and formaldehyde in the proportion indicated by the two permanganate titration figures, *i.e.*, approximately 90% of acetaldehyde to 10% of formaldehyde, and at a comparable dilution to the distillate readily showed formaldehyde by Denigès' test. Furthermore, *s*-dihydroxydimethyl peroxide distilled from *N*-sulphuric acid gave formaldehyde in the distillate.

*Action of Acetaldehyde on Natural Ether Peroxides.*—Several c.c. of acetaldehyde were added to 100 c.c. of ethers B and X, and the solutions kept over sodium sulphate. The aldehyde : hydrogen peroxide ratio was then determined in the usual way. For ether B, the ratios found were 2.1 : 1 and 2.3 : 1 and for ether X, 2.2 : 1.

*Ratio of Acetaldehyde to Hydrogen Peroxide in Treated Peroxidic Ethers.*—Two other Winchester-quart bottles of methylated ether rich in peroxides were also available and the ethers were submitted

to an initial purification. Each was slowly distilled, through a long 8-bulb pear column to prevent loss of peroxides, until the residual volume was 250 c.c. This was extracted rapidly with saturated sodium hydrogen carbonate solution to remove acids and then 40 to 50 successive small portions of water, each 10 c.c. The ether was then dried over freshly ignited sodium sulphate, and the aldehyde : hydrogen peroxide ratio determined on evaporated samples in the same way as described above. For ether A, the ratio was 1.16 and 1.13 and for ether C, 1.28. These figures confirm those obtained on untreated ethers.

*Effect of Washing on the Acetaldehyde : Hydrogen Peroxide Ratio of Natural Peroxidic Ether.*—Ether B (100 c.c.) was extracted rapidly three times with 10 c.c. of water each time. The aqueous layers were combined, made up to 50 c.c., and analysed in the usual way : the ratio of acetaldehyde to hydrogen peroxide was 1.43 : 1.

*Distribution of Acetaldehyde between Ether and Water.*—A standard solution of acetaldehyde in water, when analysed by direct addition to standard sulphite solution, was found to contain 0.256 g. in 50 c.c. Of this, 40 c.c. were added to 40 c.c. of pure diethyl ether in a graduated stoppered cylinder and the mixture was shaken and allowed to attain equilibrium at 20°. The final volumes were 43.0 c.c. of aqueous layer and 36.5 c.c. of ethereal layer. Of each, 10 c.c. were removed and the aldehyde content was determined by direct treatment with sulphite. The total amounts of aldehyde found in the two layers were in close agreement with that originally present. The ratio acetaldehyde in water to acetaldehyde in ether was 2.45 : 1.

*Distribution of Di- $\alpha$ -hydroxyethyl Peroxide between Ether and Water.*—Ether (10 c.c.) containing synthetic di- $\alpha$ -hydroxyethyl peroxide and a slight excess of acetaldehyde was shaken at 25° with 8 c.c. of water. The resultant volumes were each 8 c.c., and 5 c.c. of each were removed and the peroxide content was estimated by permanganate. The ether consumed 8.96 c.c., and the water 5.82 c.c., of *N*/10-permanganate, whence the distribution coefficient for di- $\alpha$ -hydroxyethyl peroxide is 1.5 in favour of ether.

*s-Dihydroxydimethyl Peroxide, OH·CH<sub>2</sub>·O·O·CH<sub>2</sub>·OH.*—Formalin (6 c.c.) was diluted with water (18 c.c.), and perhydrol (4.5 g.) in 12 c.c. of water added. The solution was kept for 12 hours and then allowed to evaporate rapidly in a vacuum desiccator over sulphuric acid. Crystals separated on the sides of the dish and when the volume had been reduced to 2 or 3 c.c. the contents were inoculated with the crystals and kept at 0° for a few hours. *s*-Dihydroxydimethyl peroxide separated in triangular prisms, which were separated by decantation and dried on porous plate. It is very soluble in water and in agreement with the observations of Wieland and

Wingler gives no immediate reaction with Schiff's reagent, acid permanganate, or vanadic acid. It reacts with the guaiacum and benzidine reagents only on addition of peroxidase. For analysis, 0.381 g. was dissolved in 10 c.c. of water and treated with 10 c.c. of *N*-potassium hydroxide, followed by 10 c.c. of 10-volume hydrogen peroxide solution. After 15 minutes the unconsumed alkali was titrated with standard acid. The percentage of formaldehyde found was 63.5 (calc., 63.8). This confirms the view that there are two molecules of formaldehyde combined with one of hydrogen peroxide. The crystalline solid when kept in a tube develops formic acid, but if left on an open watch-glass the crystals soon disappear through volatilisation.

*Stability of Hydrogen Peroxide in Boiling N-Sulphuric Acid and its Volatility in Steam.*—A determination was made to ascertain the loss which occurred on distillation of weak solutions of hydrogen peroxide in *N*-sulphuric acid. Of such a standard solution, 50 c.c. were distilled for 20 minutes through the usual apparatus fitted with an anti-splash device, the volume diminishing by a third to a half. On determining the peroxides in the two fractions, distillate and residue, 1.9% was found in the distillate and 2.1% had been destroyed. In a duplicate experiment with 0.5*N*-sulphuric acid, the volatile peroxide was 0.6% and that destroyed 3.6%.

*Acidity of Peroxidised Ethers.*—The presence of acetic acid in ether that has undergone autoxidation was observed by Richardson and Fortey (P., 1896, 165), but the formation of formic acid appears to have been overlooked. The latter can readily be detected by its very pungent odour and by its reducing properties on mercuric chloride, mercuric acetate or silver nitrate solution. Attempts to estimate the relative proportion of acetic and formic acids by use of methods depending on the formation of mercurous acetate or chloride proved untrustworthy. The total acidity in comparison with the peroxide content was determined on two ethers which had undergone autoxidation for several years. For ether B, 10 c.c. required 2.74 c.c. of *N*/10-sodium hydroxide for neutralisation to phenolphthalein and the peroxide content was equivalent to 28.9 c.c. of *N*/10-permanganate. If the acidity arises entirely from the oxidising action of hydrogen peroxide on aldehydes, this corresponds to a 15.9% conversion of hydrogen peroxide. For ether X, 10 c.c. required 0.72 c.c. of *N*/10-sodium hydroxide and the peroxides required 19.8 c.c. of *N*/10-permanganate. This corresponds to a 6.8% conversion of hydrogen peroxide. Whether the formic acid arises by oxidation of methylated ethers present in the original ether or by oxidation of the vinyl alcohol form of acetaldehyde is not known.

*The Guaiacum and Benzidine Tests for Peroxides.*—For these tests a freshly prepared 10% alcoholic tincture of guaiacum and a 1% solution of benzidine in 50% alcohol were used. Pure crystalline dihydroxydimethyl peroxide in aqueous solution gives no coloration on addition of the guaiacum or benzidine reagent, but a blue colour is immediately produced on addition of a dilute solution of peroxidase (from horse-radish) to either. Di- $\alpha$ -hydroxyethyl peroxide obtained as a syrup by evaporation of an ethereal solution of the components containing a slight excess of acetaldehyde gives no coloration in aqueous solution with the same reagents, but does so on addition of peroxidase. Fresh aqueous solutions of formaldehyde or acetaldehyde and hydrogen peroxide in the ratio 2 : 1, however, both give a direct reaction with the benzidine reagent without the use of peroxidase, but not with guaiacum. In both cases this reaction becomes negative when the solutions are kept for 2 or 3 days. A similar direct benzidine reaction is obtained when a natural peroxidic ether is evaporated and the aqueous solution of the residual peroxide tested with the benzidine reagent.

The results are consistent with the view that the direct blueing of benzidine is due to an intermediate peroxide containing the aldehyde and hydrogen peroxide in molecular proportion.

Laboratory samples of heptaldehyde and benzaldehyde suspended in water gave the direct benzidine reaction without addition of hydrogen peroxide, owing to their content of peroxides. It is also of interest that butyl, isooctyl and amyl alcohols gave a reaction for peroxides with benzidine or guaiacum and peroxidase, but the reaction was not shown by methyl, ethyl, isopropyl and benzyl alcohols. In many of these reactions the enzyme peroxidase can be replaced by a drop of a solution of a ferrous or ferric salt.

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[Received, February 2nd, 1929.]

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