[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

The Autoxidation of Certain Ethylene Oxides

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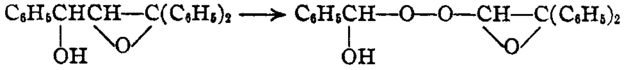
In a recent paper we reported that when α,α-diphenyl-β-(hydroxybenzyl) ethylene oxide is exposed to the air it is oxidized to a peroxide.[1]

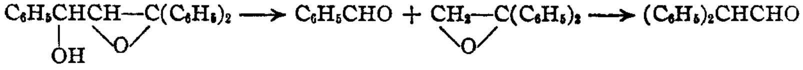


$$C_6H_5\underset{\displaystyle OH}{\underset{|}{C}}H\underbrace{CH{-}C}_{O}(C_6H_5)_2 \longrightarrow C_6H_5\underset{\displaystyle OH}{\underset{|}{C}}H{-}O{-}O{-}\underbrace{CH{-}C}_{O}(C_6H_5)_2$$

This peculiar case of autoxidation first aroused our interest because it was erratic, some specimens apparently being perfectly stable in the air while others, which had been prepared in the same manner, were oxidized with sufficient rapidity to cause a perceptible rise in temperature. Another incentive to further investigation appeared when the structure of the oxidation product was definitely established, showing that the substance is a peroxide of the type that is usually obtained from free radicals.

We have found that the erratic character of the oxidation is not due to differences in the purity of the oxide but to variations in the quality of the air. No oxidation occurs either in air containing a trace of ammonia or in air that has been washed with bases, but when a little hydrogen chloride is added to the washed air, oxidation starts after a time and the principal product is the peroxide. The odor of benzaldehyde is perceptible whenever oxidation occurs, and benzoic acid, benzophenone and formic acid are always formed along with the peroxide.

We have found also that, in all probability, the function of the acid is to cleave the oxide—a rather surprising role in a reaction between a gas and a solid. In solutions containing a trace of base the oxide can be preserved indefinitely but in solutions containing even traces of acid it is rapidly destroyed in accordance with the equation

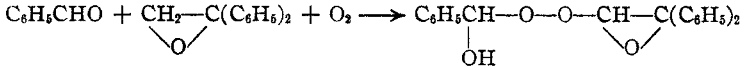


$$C_6H_5\underset{\displaystyle OH}{\underset{|}{C}}H\underbrace{CH{-}C}_{O}(C_6H_5)_2 \longrightarrow C_6H_5CHO + \underbrace{CH_2{-}C}_{O}(C_6H_5)_2 \longrightarrow (C_6H_5)_2CHCHO$$

This transformation is complete and the process cannot be reversed either in the presence or the absence of a solvent. In solutions containing equivalent quantities of benzaldehyde and diphenylethylene oxide and a trace of base, both the aldehyde and the oxide slowly disappeared but no oxido alcohol was formed. When a solution of diphenylethylene oxide in an equivalent quantity of benzaldehyde was left to itself in an atmosphere of nitrogen, no change whatsoever occurred in the course of a month. When the solution was heated on a steam-bath the oxide slowly changed to diphenyl acetaldehyde but there was no condensation of the oxide and the aldehyde, and the addition of a few bubbles of hydrogen chloride merely accelerated the rearrangement of the oxide. But when a similar solution of

[1] Kohler, Richtmyer and Hester, THIS JOURNAL, **53**, 205 (1931).

the oxide in the aldehyde was exposed to the air it soon began to deposit a solid and it ultimately solidified completely. Under favorable conditions the solid contained nearly 50% of the possible amount of the peroxide, mixed with smaller quantities of the mono benzoate of diphenyl glycol, benzoic acid, benzophenone and formic acid. Here the peroxide is manifestly formed from the primary cleavage products of the oxide in accordance with the equation

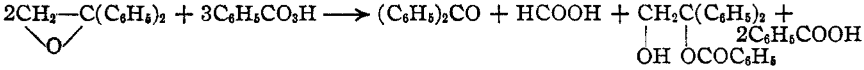


$$C_6H_5CHO + \underset{\diagdown O \diagup}{CH_2-C(C_6H_5)_2} + O_2 \longrightarrow \underset{OH}{C_6H_5CH}-O-O-\underset{\diagdown O \diagup}{CH-C(C_6H_5)_2}$$

In this manner it was established that the oxide is not attacked by oxygen in the absence of acid, that acids cleave the oxide to benzaldehyde and diphenylethylene oxide, that the oxido alcohol cannot be regenerated from these cleavage products, and that in the air these primary cleavage products are oxidized to the peroxide. The conclusion seems inevitable that the peroxide is formed in a series of reactions involving, first, cleavage of the oxide by acid, then autoxidation of the primary cleavage products, and finally synthesis of the peroxide from the products of oxidation.

The nature of the oxidation products from which the peroxide is formed is still somewhat mysterious. Diphenylethylene oxide is not attacked by free oxygen either in the presence or in the absence of acids. Benzaldehyde readily undergoes autoxidation being converted, first, into benzoperacid and finally into benzoic acid under all conditions hitherto investigated. Both of these oxidation products react with diphenylethylene oxide at the ordinary temperature but the reactions do not lead to the peroxide.

The reaction between benzoperacid and diphenylethylene oxide has been investigated with care by Meerwein and Bodendorf.[2] It is represented by the equation



$$2\underset{\diagdown O \diagup}{CH_2-C(C_6H_5)_2} + 3C_6H_5CO_3H \longrightarrow (C_6H_5)_2CO + HCOOH + \underset{OH\ \ OCOC_6H_5}{CH_2C(C_6H_5)_2} + 2C_6H_5COOH$$

As will be seen, this reaction accounts for approximately half of the material and nearly all of the products that are formed in the autoxidation of the mixture of benzaldehyde and diphenylethylene oxide, but it does not account for the peroxide.

The experimental conditions under which the reaction was studied were quite different from those under which the peroxide is formed but differences in the experimental conditions could hardly account for oxidation to open chained compounds in the one case and the formation of the peroxide, in which the oxide ring is intact, in the other. Evidently benzoperacid—like benzoic acid—readily opens the oxide ring; after that has happened, the formation of the peroxide is impossible. For these reasons it seemed to us highly improbable that benzoperacid was an intermediate in the forma-

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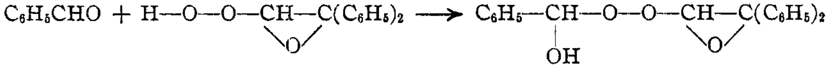
[2] Bodendorf, Dissertation, Königsberg, 1928.

tion of the peroxide, but we nevertheless decided to repeat the work of Bodendorf under conditions as nearly as possible like those which prevailed in the autoxidation of the cleavage products. To this end we prepared nearly pure benzoperacid by the method of Smit[3] and added it very slowly, in an atmosphere of nitrogen, to a solution of the oxide in benzaldehyde. The products were the same as those obtained by Bodendorf; no peroxide could be detected at any stage of the operation.

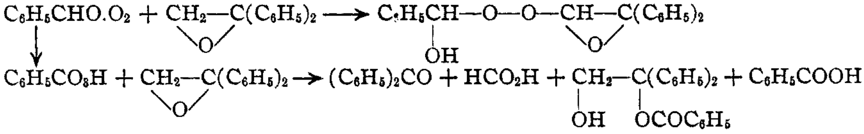
From the foregoing facts it is certain that benzoperacid is not an intermediary in the formation of the peroxide. In form and in behavior this peroxide most nearly resembles the monohydroxy dialkyl peroxides which are obtained by the addition of alkyl hydroperoxides to aldehydes.[4] In the case under consideration this mode of formation would be represented by the equation



$$C_6H_5CHO + H{-}O{-}O{-}\underbrace{CH{-}C}_{O}(C_6H_5)_2 \longrightarrow C_6H_5{-}\underset{OH}{\underset{|}{CH}}{-}O{-}O{-}\underbrace{CH{-}C}_{O}(C_6H_5)_2$$

Here the intermediary is a derivative of hydrogen peroxide which could not be formed under the conditions of the experiment.

There remains only the possibility that benzoperacid does not represent the primary oxidation product of benzaldehyde. This possibility has often been discussed in connection with observations that newly oxidized benzaldehyde is a more powerful oxidizing agent than benzoperacid[5] but no positive evidence of such a product has hitherto been obtained. It seems not improbable, however, that oxidation of a concentrated solution of the oxide in benzaldehyde, or of the intimate mixture of the aldehyde and the oxide that would be formed by cleavage on the surface of the solid oxido alcohol, would present an unusually favorable condition for catching some of the moloxide before its rearrangement to the peracid. Such an energetic, neutral antecedent of the peracid would account both for the peroxide and for the other oxidation products that are always formed at the same time



$$\begin{array}{l} C_6H_5CHO.O_2 + \underbrace{CH_2{-}C}_{O}(C_6H_5)_2 \longrightarrow C_6H_5\underset{OH}{\underset{|}{CH}}{-}O{-}O{-}\underbrace{CH{-}C}_{O}(C_6H_5)_2 \\ \downarrow \\ C_6H_5CO_3H + \underbrace{CH_2{-}C}_{O}(C_6H_5)_2 \rightarrow (C_6H_5)_2CO + HCO_2H + \underset{OH}{\underset{|}{CH_2}}{-}\underset{OCOC_6H_5}{\underset{|}{C}}(C_6H_5)_2 + C_6H_5COOH \end{array}$$

Experimental

All the oxide used in the investigation was isolated and purified in the same manner. It was prepared in quantity as directed in the earlier paper and left in the alkaline solu-

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[3] Smit, *Rec. trav. chim.*, **49**, 676 (1930).

[4] Rieche, *Ber.*, **63**, 2642 (1930).

[5] (a) Engler and Weissberg, "Kritische Studien über die Vorgängen der Autoxidation," 1904, p. 91; (b) Baeyer and Villiger, *Ber.*, **33**, 1569 (1900); (c) Staudinger, *ibid.*, **46**, 3530 (1913); (d) Jorissen and Van der Beek, *Rec. trav. chim.*, **46**, 42 (1927); (e) Milas, *J. Phys. Chem.*, **33**, 1204 (1929).

tion until it was needed. A suitable quantity was then precipitated with ice water, rapidly washed and dried, and recrystallized from ether and petroleum ether.

Oxidation.—For the purpose of determining all the products of oxidation, three lots of 5 g. each were exposed to the air in thin layers at the bottom of large Erlenmeyer flasks until the odor of benzaldehyde had disappeared completely. The average gain in weight was 6.2%. The resulting solids were cooled in a freezing mixture and washed, repeatedly, with small quantities of equally cold ether, which removed about 20% of the material. From the ethereal solution sodium bicarbonate extracted formic acid—recognized by its reducing action on mercuric oxide—and benzoic acid which was identified in the usual manner. The ethereal layer, on distillation, left an oil which solidified almost completely when it was inoculated with benzophenone, and which formed a phenylhydrazone melting at 137°. The ethereal extract therefore contained formic acid, benzoic acid and benzophenone.

The solid was recrystallized from acetone and ether; it contained two substances: the peroxide which had been obtained before in the same manner and a small quantity of another compound which crystallized in needles and melted at 156°.

Anal. Calcd. for $C_{21}H_{18}O_3$: C, 79.2; H, 5.7. Found: C, 79.0; H, 5.8.

This substance is the monobenzoate of diphenyl glycol which was first obtained by Bodendorf by oxidizing diphenylethylene oxide with benzoperacid. Bodendorf assumed, perhaps correctly, that the peracid first combines with the oxide to form the corresponding perbenzoate, and that this substance is subsequently reduced to the benzoate. But the course of the reaction may be quite different because the benzoate is also formed very readily by simply dissolving benzoic acid in the melted oxide. The ratio between the amounts of peroxide and other oxidation products was not constant, the yields of peroxide varying between 70 and 80%.

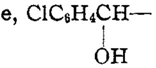
Conditions Essential for the Formation of the Peroxide.—In a search for conditions more favorable for investigating the mechanism of the oxidation we passed air for twenty-four hours through neutral solutions of the oxide in alcohol, ether, acetone and benzene, but in no case obtained any oxidation. In faintly acid solutions there was a very slow oxidation but no peroxide was formed; after seventy-two hours, benzoic and diphenylacetic acids were the only oxidation products which could be detected.

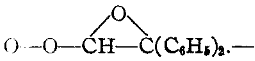
In order to ascertain the importance of acid, three portions of the same preparation of the oxide were placed in large vacuum desiccators which were first exhausted, then filled—the one with air that had been passed through very dilute ammonia, the second with air which had been passed through sodium hydroxide—and the third with air that had been passed first through sodium hydroxide and then through moderately dilute hydrochloric acid. After five days only the third sample had been oxidized, the crystals of the first and second still retaining both their shape and their luster.

Autoxidation of the Cleavage Products.—A large number of solutions of diphenylethylene oxide in benzaldehyde were oxidized both in air and in oxygen. Peroxide was formed in every experiment but in many cases the amount was small and we failed to find any conditions under which the yield was equal to that which had been obtained from the oxido alcohol. Thus, in a typical experiment a solution of 2.5 g. of diphenylethylene oxide in 1.4 g. of benzaldehyde was exposed to the air in a large Erlenmeyer flask. After five hours solid began to appear and after two days the odor of benzaldehyde had disappeared completely. The resulting solid, manipulated like the product from the oxido alcohol yielded 1.8 g. of peroxide, 0.76 g. of the monobenzoate of diphenyl glycol and smaller quantities of benzoic acid and benzophenone.

Oxidation of the Cleavage Products with Benzoperacid.—A solution of the sodium salt of benzoperacid, prepared by the method of Smit, was acidified in a dropping funnel which was surrounded with ice water. At intervals small quantities of the resulting liquid acid were drawn into a solution of 2.5 g. of diphenylethylene oxide in 1.4 g. of benzaldehyde which was likewise cooled with ice water and which was kept in an atmosphere of nitrogen. After twenty-four hours the mixture was a solid free from benzaldehyde. By the usual manipulation, this solid yielded the monobenzoate of diphenyl glycol, benzoic acid and benzophenone, but no peroxide could be detected.

Autoxidation of *o*-Chlorobenzaldehyde and Diphenylethylene Oxide,

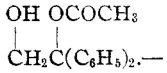




$\mathrm{ClC_6H_4\underset{OH}{CH}-O-O-\overbrace{CH-C}^{O}(C_6H_5)_2}$.—In search of a system more favorable for an investigation of the mechanism of autoxidation, we examined the behavior of solutions of diphenylethylene oxide in a few other aldehydes. A solution of 2 g. of the oxide in 1.5 g. of *o*-chlorobenzaldehyde remained liquid after exposure to the air for several days, but solidified in the course of a week. After extraction with ether, there remained 0.9 g. of a solid which decomposed briskly at the melting point. This solid was recrystallized from acetone and ether from which it separated in very thin needles melting at 140–141° with evolution of gas.

Anal. Calcd. for $C_{21}H_{17}O_4Cl$: C, 68.4; H, 4.7. Found: C, 68.1; H, 4.8.

Autoxidation of Acetaldehyde and Diphenylethylene Oxide,

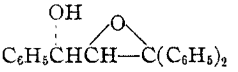


$\mathrm{\overset{OH}{CH_2}\overset{OCOCH_3}{C}(C_6H_5)_2}$.—Various solutions of diphenylethylene oxide in acetaldehyde were exposed to the air until they had solidified completely. No peroxide could be detected in any of them; the principal product in every case was the monoacetate of diphenyl glycol, which separates from ether and petroleum ether in large prismatic crystals, and melts at 91°.

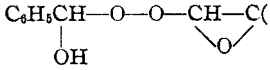
Anal. Calcd. for $C_{16}H_{16}O_3$: C, 75.0; H, 6.2. Found: C, 74.8; H, 6.6.

Summary

The autoxidation of the oxido alcohol



$\mathrm{C_6H_5\overset{OH}{C}H\overbrace{CH-C}^{O}(C_6H_5)_2}$ to the peroxide



$\mathrm{C_6H_5\underset{OH}{C}H-O-O-\underbrace{CH-C}_{O}(C_6H_5)_2}$, in all probability involves first cleavage to benzaldehyde and diphenylethylene oxide, then autoxidation of the benzaldehyde, and finally synthesis of the peroxide from the autoxidation product of the aldehyde and diphenylethylene oxide. The intermediate in this synthesis is not benzoperacid; it appears to be an unstable "moloxide" antecedent to the peracid.

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