[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY, UNIVERSITY OF MINNESOTA]

STUDIES IN AUTO-OXIDATION. I. CYCLOHEXENE PEROXIDE. (PRELIMINARY COMMUNICATION)[1]

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The formation of peroxides, or moloxides, as intermediate products in auto-oxidation processes was suggested almost simultaneously, in 1897, by the theory of Bach[2] and that of Engler and Wild.[3] Although in some cases experimental confirmation of their views has not been as specific as might be desired, their fundamental ideas have grown in favor up to the present time. In numerous cases of substances undergoing auto-oxidation, tests characteristic of peroxides have been obtained, but in nearly all cases the isolation of the particular substances responsible for these tests has not been realized. One notable exception is offered by the intermediate product in the oxidation of benzaldehyde, which was recently isolated by Jorissen and Van der Beek.[4] Although this substance, benzoyl hydroperoxide, had been known for some years,[5] previous attempts to isolate it in the auto-oxidation of benzaldehyde had resulted in failure.

In the case of substances containing the ethenoid linkage, the isolation of intermediate peroxides has presented still more difficulty, and repeated failures by various investigators to isolate these products have gradually strengthened the view that the primary auto-oxidation products are unisolable. Substances which corresponded in empirical composition to peroxides have been isolated by Engler and Frankenstein[6] and Staudinger[7] but in neither case were the characteristic reactions of peroxides shown. According to Staudinger, his product was formed from the monomolecular peroxide by polymerization, through oxygen-to-oxygen linkages, to a product of indefinitely large molecular weight.

For complete confirmation of the theory of peroxide formation, it is, of course, necessary to isolate the primary intermediate products, and with this end in view the present research was started about four years ago. In choosing an unsaturated hydrocarbon for use as a starting material the main requisites were simplicity of structure and reasonable activity toward gaseous oxygen and it was found that cyclohexene fulfilled the

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[1] This paper describes the first of a series of investigations on the auto-oxidation of substances containing the ethenoid linkage, the primary purpose being a study of the mechanism of these reactions.

[2] Bach, *Compt. rend.*, **124**, 951 (1897).

[3] Engler and Wild, *Ber.*, **30**, 1669 (1897).

[4] Jorissen and Van der Beek, *Rec. trav. chim.*, **45**, 245 (1926).

[5] Baeyer and Villiger, *Ber.*, **33**, 858, 1569 (1900).

[6] Engler and Frankenstein, *Ber.*, **34**, 2933 (1901).

[7] Staudinger, *Ber.*, **58**, 1075 (1925).

latter requirement to a greater extent than the simple, open chain hydrocarbons.

Continuous bubbling of oxygen through this hydrocarbon was obtained by means of a circulator previously described by the writer.[8] By this means exposure of a fresh surface of liquid was assured at all times. Oxidation was carried out at room temperature under an average pressure of about 1 atmosphere of oxygen and the duration of experiments varied between one and four months.

The crude product of oxidation in each case showed only a faint yellow coloration and its viscosity varied with the time of oxidation. It was at once noted that the liquid gave a pronounced peroxide reaction but it was evidently a mixture containing a considerable amount of unchanged cyclohexene. After distilling the latter off under reduced pressure, a sirupy residue was obtained from which it was attempted to separate the peroxide. After several unsuccessful attempts it was found that the liquid showed very little tendency to decompose on moderate heating, so distillation under very low pressures was attempted. By using a pressure of about 0.5 mm., it was found that even early in the distillation a peroxide test was given by the distillate. By following the intensity of the color produced by one drop of the distillate with 2 cc. of titanic sulfate solution, the fraction richest in peroxide was secured and this submitted to further fractional distillation. Finally a liquid was obtained which boiled, under 0.5 mm. pressure, at 54–56°. The quantities of this liquid, obtained from various experiments, were always very small, the largest amount being approximately 6 g. This latter amount was the product from 800 g. of cyclohexene which had been oxidized over a period of four months.

Cyclohexene peroxide is a colorless, mobile liquid with a pungent odor strongly reminiscent of oxidizing substances such as ozone, nitrogen pentoxide, hypochlorous acid, etc. It has a corrosive action on the skin, which manifests itself after contact for only a few seconds. If allowed to remain on the skin for some time, it produces burns which take several days to heal. The peroxide colors titanic sulfate solution instantly, liberates iodine from acidified potassium iodide and decolorizes indigo solution; in brief, it behaves as a typical organic peroxide. Analysis of the peroxide gave values as follows.

Anal. Calcd. for $C_6H_{10}O_2$: C, 63.16; H, 8.77. Found: C, 63.26, 63.22; H, 8.88, 8.86.

A molecular weight determination in benzene, by the Maass modification of the Beckmann cryoscopic method,[9] gave a value of 119, while the theoretical value is 114. Determination of active oxygen iodimetrically was unsatisfactory, as the liberated iodine apparently reacted with the reduc-

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[8] Stephens, *Ind. Eng. Chem.*, **19**, 425 (1927).

[9] Maass, *Trans. Roy. Soc.* (*Canada*) **13**, Sec. iii, 97 (1919).

tion product. Reduction with stannous chloride also failed to give the expected results but the values obtained by the latter method were concordant. Analysis of three different samples of peroxide gave values corresponding to 78.7 – 79.8% of the theoretical amount of active oxygen. The agreement between these different analyses must indicate either a constant amount of impurity or a constant amount of side reactions during reduction. The latter does not seem very plausible, as one would expect slight variations in technique to cause variations in the extent of side reactions.

The analytical values for carbon and hydrogen require that any impurity present have the same composition as the peroxide and there are two possible ways of accounting for the existence of such an impurity. First, polymerization or some similar reaction may take place in the vapor phase and the impurity may thus be carried over into the distillate. Second, if we accept the existence of two modifications of the peroxide,[10] one labile and one stable, we might assume that their boiling points were so close together as to render them inseparable by distillation. The possibility of the existence of two forms of cyclohexene peroxide is one which will be studied in this Laboratory in the near future.

The other possibility, that of polymerization, is one which has already been investigated in a preliminary way. After each fractionation of cyclohexene peroxide, it was noticed that a considerable residue of sirupy liquid remained which could not be distilled. An examination of the empirical composition of this liquid showed it to be practically identical with the peroxide.

Anal. Calcd. for $C_6H_{10}O_2$: C, 63.16; H, 8.77. Found: C, 63.17, 62.58; H, 8.46, 8.53.

Determination of the molecular weight in benzene as above, gave a value of 215, whereas $(C_6H_{10}O_2)_2$ requires 228. It seems probable, then, that at the temperature of distillation, two molecules of peroxide may combine, by polymerization or condensation, to form a product or products of the same empirical composition. It is rather interesting to note, in passing, that Harries[11] obtained two ozonides of cyclohexene, only one of which was distillable.

In examining further the sirupy liquid obtained from the peroxide, it was found that, although it produced no coloration of titanic sulfate at room temperature, except after long contact, a strong color developed on heating the mixture. As the substance is very slightly soluble in water, the function of the heat may be to increase the solubility or to cause the dissociation of an unstable polymer. If this product were a single substance, formed from two molecules of peroxide, it would be expected that one peroxide group would be left as such and therefore one would ex-

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[10] Staudinger, *J. prakt. Chem.*, **85**, 330 (1912).

[11] Harries, *Ann.*, **410**, 25–26 (1915).

pect to find 1/2 the amount of active oxygen required by the monomolecular form. The actual value obtained was 34% instead of 50% but, as will be brought out in detail in later papers, there are possible reactions which would use up active oxygen without changing the empirical composition and there is no reason for believing the sirupy liquid to be the product of a single reaction. However, the existence in the product of a considerable proportion of a substance having peroxide properties seems to point to the possibility of a condensation of two molecules of the simple peroxide, in which one peroxide group is left as such. This would involve an entirely different type of reaction from that postulated by Staudinger to account for his polymeric peroxide.

Investigations in this field are being extended along a number of different lines and further communications will be published in the near future.

Summary

1. For the first time, a true peroxide has been isolated as a product of auto-oxidation of an unsaturated hydrocarbon. Thus, specific confirmation has been obtained for the Bach-Engler interpretation of the action of oxygen on the ethenoid linkage.

2. Evidence has been obtained which shows that there is a tendency for two molecules of peroxide to combine, forming a new substance with peroxide properties.

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A PREPARATION METHOD FOR BENZOPHENONE

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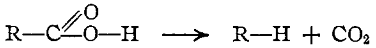
Introduction and Discussion

It is well known that simple carboxylic acids yield hydrocarbons to a greater or less extent when they are heated with finely divided metals, particularly copper and nickel.



$$\mathrm{R{-}\overset{\overset{O}{/\!\!/}}{C}{-}O{-}H \longrightarrow R{-}H + CO_2}$$

In the case of aliphatic acids the reaction is usually difficult to effect. Acetic acid, for example, when heated with copper at 390–411°, gives mainly acetone and when nickel is used as the catalyst a considerable portion of the acid is decomposed into complex carbonaceous substances.[1] With aromatic acids the decomposition is usually easier but frequently, as with benzoic acid and nickel,[2] the reaction temperature is so high that the resulting hydrocarbons are largely transformed into other substances.

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[1] Sabatier and Senderens, *Ann. chim. phys.*, [8] **4**, 467 (1905).

[2] Sabatier and Mailhe, *Compt. rend.*, **159**, 217 (1914).