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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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF PRINCETON UNIVERSITY]

A PREPARATION METHOD FOR BENZOPHENONE

BY GREGG DOUGHERTY

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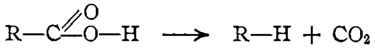
Introduction and Discussion

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.



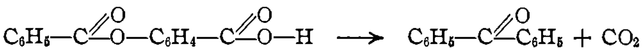
$$R{-}C(=O){-}O{-}H \longrightarrow R{-}H + CO_2$$

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.

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

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

It has been found that this process of eliminating carbon dioxide from an acid can be used to advantage in the preparation of benzophenone from *o*-benzoylbenzoic acid.



$$C_6H_5-C\overset{/\!\!/O}{\diagdown}O-C_6H_4-C\overset{/\!\!/O}{\diagdown}O-H \longrightarrow C_6H_5-C\overset{/\!\!/O}{\diagdown}C_6H_5 + CO_2$$

The yields, 80–90% of the theoretical, exceed the average of those obtained by the Friedel and Crafts synthesis, in which benzene and benzoyl chloride react in the presence of aluminum chloride, by about 10%. Furthermore *o*-benzoylbenzoic acid, which is the intermediate in the synthetic anthraquinone process, is manufactured on a large scale and should be obtained without difficulty. It can also be prepared easily and inexpensively from phthalic anhydride, benzene and aluminum chloride.[3] This reaction goes nearly to completion, 95–97%, so that the yield of benzophenone based on the phthalic anhydride is still somewhat better than that obtained when benzoyl chloride and benzene are used, and the cost of the materials is much less.

When *o*-benzoylbenzoic acid is heated alone to about 300° some carbon dioxide is eliminated and benzophenone can be detected among the products. The yield, however, is negligible. The catalysts which accelerate the reaction most efficiently are metals such as copper, nickel, iron and the *o*-benzoylbenzoic acid salts of these metals. It is not necessary that the metals be particularly finely divided as they go into solution in the acid, and the only apparent advantage in having a fine state of subdivision is to increase the rate of solution. The preferred catalysts are finely divided copper and the copper salt of *o*-benzoylbenzoic acid. The latter is easily made by adding a copper sulfate solution to a solution of the sodium salt of the acid, washing, filtering and drying the precipitate at 110°. The velocity of the reaction increases with the amount of catalyst used, but too large a quantity causes inconvenience in getting out the product. It has been found that a satisfactory ratio is 1-3 g. of copper, or an amount of the copper salt of *o*-benzoylbenzoic acid containing an equivalent weight of copper, to 100 g. of the acid. In the presence of these catalysts carbon dioxide elimination begins at about 150° and increases as the temperature rises until 306° is reached, when the reaction mixture begins to boil. The speed of the reaction below 200° is too slow for practical purposes and above 280° there is decomposition, the formation of anthraquinone and unidentified tarry substances. The optimum temperature range is about 250–270°.

Preparation Procedure

Three hundred grams of pure *o*-benzoylbenzoic acid was placed in a distilling flask with a low side tube. To this was added 20 g. of the copper salt of the acid. The flask was fitted with a mechanical stirrer

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[3] Cain, "The Manufacture of Intermediate Products for Dyes," Macmillan and Co., London, **1918**, p. 240.

arranged through a mercury seal, and a thermometer the bulb of which was immersed in the liquid when the material melted. The mixture was heated with stirring; carbon dioxide evolution was appreciable at 200°, and it was allowed to escape through the side tube of the flask and to bubble through water, which gave an indication of the progress of the reaction. The temperature was allowed to rise and was maintained at 260° until carbon dioxide evolution ceased (about four hours). It is necessary to continue until the carbon dioxide evolution has completely stopped. If a distillation is attempted before this point, a considerable quantity of anthraquinone is formed, which contaminates the product. The stirrer was taken from the flask, a short air condenser attached to the side tube and the thermometer raised out of the liquid as for distillation. The crude benzophenone was distilled over until the drops of distillate became dark in color; the weight of this crude product was 209 g., 86.6% of the theoretical. One crystallization from 95% alcohol gave pure benzophenone, m. p. 47–48°, in an amount corresponding to 82–84% of the theoretical based on the *o*-benzoylbenzoic acid. The crystallization may be replaced by distillation in a vacuum.

Summary

A method for the preparation of benzophenone has been described.

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[CONTRIBUTION FROM THE RESEARCH LABORATORIES OF PARKE, DAVIS AND CO.]

THE ACTIVE PRINCIPLES OF THE POSTERIOR LOBE OF THE PITUITARY GLAND.[1] I. THE DEMONSTRATION OF THE PRESENCE OF TWO ACTIVE PRINCIPLES. II. THE SEPARATION OF THE TWO PRINCIPLES AND THEIR CONCENTRATION IN THE FORM OF POTENT SOLID PREPARATIONS

BY OLIVER KAMM, T. B. ALDRICH, I. W. GROTE, L. W. ROWE AND E. P. BUGBEE

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Introduction

The manifold physiological activities of extracts of the posterior lobe of the pituitary gland are now well known; namely, their effect in stimulating uterine contractions (oxytocic activity), their ability to raise the blood pressure (pressor activity), and their diuretic-antidiuretic effects (renal activity). These three types of activity have led the way to three definite and important medical applications; these are illustrated respectively by the use of pituitary solutions in obstetrics, in the treatment of surgical shock, and in the control of diabetes insipidus.

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[1] Presented before the Detroit meeting of the American Chemical Society, September, 1927.