

The Preparation of Benzoyl Hydrogen Peroxide

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In the investigation of unsaturated hydrocarbons of the ethylene type by oxidation, there has been great need of a method of oxidation which will give good yields of product and which is not likely to cause rearrangement of the carbon structure. Oxidation by ozone has been the most useful method, although it is difficult to prepare more than one or two grams of ozonide per day except with a very excellent ozone generator. The method of treating an olefin with benzoyl hydrogen peroxide to form the oxide, first carried out by N. Prileschajew,¹ has given excellent results in this Laboratory in the investigation of petroleum olefins and the method would undoubtedly have had much wider application except for the difficulty of preparing this reagent. L. Ruzicka, H. Silberman and M. Furter² have shown that this reagent reacts quantitatively with certain hydrocarbons that resist catalytic hydrogenation.

We have also found that this reagent can be used to measure the olefin unsaturation in cracked petroleum products, lubricating oils and the like, where hydrogenation is difficult or impossible due to the presence of sulfur compounds, and where the determination of iodine or bromine numbers may be unreliable.

The original method for the preparation of benzoyl hydrogen peroxide, described by Baeyer and Villiger,³ consisted in treating an ether solution of dibenzoyl peroxide with sodium ethylate in absolute alcohol at -5° , forming ethyl benzoate and precipitating flocculent sodium perbenzoate. Water was added, the cold aqueous solution extracted several times with ether, acidified and the free acid extracted with chloroform. The yields are generally very poor, large volumes of ether are required, the extraction of the sodium salt from the ether may require several hours, and about ten to fifteen grams of the acid is all that can be expected from a good day's work. J. Lévy and M. R. Lagrave⁴ improved the method somewhat by substituting toluene for ethyl ether and H. Hibbert and C. P. Burt⁵ recommended adding the chilled solution of the sodium salt to a chilled excess of dilute sulfuric acid, but they erroneously attribute the poor yields so frequently obtained to the presence of free alkali in the solution. They state, "Benzoyl hydrogen peroxide is very unstable in the presence of alkali and its preparation must, therefore, be carried out in such a manner that there is no trace of sodium peroxide in solution when the free hydroperoxide is liberated." They attribute the loss of active oxygen during acidification to sodium ethylate carried into solution with the sodium salt

(1) Prileschajew, *Ber.*, **42**, 4811 (1909); **56**, 1803, 1805, 1808 (1923); **57**, 585 (1924).

(2) Ruzicka, Silberman and Furter, *Helv. Chim. Acta*, **15**, 482 (1932).

(3) Baeyer and Villiger, *Ber.*, **33**, 1569 (1900).

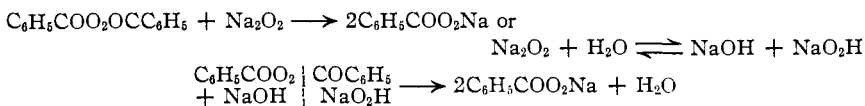
(4) Lévy and Lagrave, *Bull. soc. chim.*, **37**, 1597 (1925).

(5) Hibbert and Burt, *THIS JOURNAL*, **47**, 2240 (1925).

and "the latter during the acidification process yields sufficient free alkali to bring about a decomposition of the hydroperoxide as fast as it is formed."

A. Baeyer and V. Villiger, in their original paper, had shown by slow or partial acidification that a sparingly soluble acid salt was formed which was exceedingly unstable. This undoubtedly accounts for the loss of active oxygen noted by Hibbert and Burt, since we have found that practically the theoretical yields of the benzoyl hydrogen peroxide were obtained by acidifying solutions containing free sodium peroxide, and also no difference could be noted in the rate of decomposition, as measured by oxygen evolution, of aqueous solutions of the sodium salt with and without free sodium hydroxide. At 0° there was no appreciable decomposition in six hours; at 25° the amount of decomposition at the end of three and one-half hours was the same in each case.

We find the benzoyl hydrogen peroxide can be made with equal facility from benzoyl chloride or dibenzoyl peroxide by treating with an excess of sodium peroxide in cold aqueous solution. No solvent is required, except a small amount of chloroform to take up the free acid after acidifying. The reaction requires very little attention, and the yield is double that obtained by the Baeyer and Villiger method or any of its later modifications. The yields show that one mole of dibenzoyl peroxide gives nearly two moles of the sodium salt of benzoyl hydrogen peroxide, evidently according to the reaction



Experimental

It was noted, in the preparation of dibenzoyl peroxide in the usual way, that the crude product contained substantial proportions of a white solid, insoluble in chloroform and readily soluble in water. This was found to be the sodium salt of benzoyl hydrogen peroxide, which changes on standing at room temperature to sodium benzoate and oxygen. It was then found that by using an excess of sodium peroxide and agitating the aqueous mixture for six hours the yield of dibenzoyl peroxide was cut down to about 20% of the theoretical, based upon the benzoyl chloride used; the balance of the material was the sodium salt of the benzoyl hydrogen peroxide, in the form of the solid, white silky needles and in solution. It was found that no loss of active oxygen occurred at 0 to +5° and that satisfactory yields could be obtained by agitating the peroxide reaction mixture for six to eight hours.

Preparation from Benzoyl Chloride.—Eighty-five grams of sodium peroxide was stirred into about 650 cc. of cracked ice and water and 100 g. of benzoyl chloride added with agitation during half an hour. The mixture, after all lumps were broken up, was kept chilled to 0 to +5°, and agitated for six hours, filtered on a chilled Buchner funnel, the solid mixture quickly transferred to 700 cc. of ice water to dissolve the finely crystalline sodium salt, filtered again and the aqueous filtrates combined. The aqueous solution was then quickly added to a slight excess of 10% sulfuric acid also chilled to about 0°. Under these conditions the benzoyl hydrogen peroxide separates, not as an oil

as it does in the presence of ether and alcohol, but as a white crystalline solid. The free acid is quickly extracted with chloroform in three successive extractions. It is advantageous to add the chloroform to the sulfuric acid solution quickly so as to remove the per acid as it is liberated. The yield of the acid is readily determined by adding 5 cc. of the chloroform extract to an excess of potassium iodide solution, acidifying, and titrating the liberated iodine. In a typical experiment, as described above, the yield of dibenzoyl peroxide was 21 g. and benzoyl hydrogen peroxide 68 g. Allowing for the benzoyl chloride corresponding to the amount of dibenzoyl peroxide recovered, the yield of benzoyl hydrogen peroxide on the remaining benzoyl chloride was 91%. These results are sufficient to show that the splitting of dibenzoyl peroxide by aqueous sodium peroxide gives two moles of the sodium salt of the per acid.

The by-product dibenzoyl peroxide, which is the intermediate product in the reaction, can be employed as the original material replacing the equivalent amount of benzoyl chloride. In a typical experiment 88 g. of benzoyl chloride, 40 g. of dibenzoyl peroxide and 85 g. of sodium peroxide gave 67 g. of benzoyl hydrogen peroxide and 32 g. of dibenzoyl peroxide.

Solubility of Sodium Benzoyl Peroxide (Sodium Perbenzoate).—The solubility of the sodium salt was determined by saturating 300 cc. of water at 0° with an excess of the sodium salt, filtering quickly on a Buchner funnel and titrating a portion of the solution for active oxygen. The results show that a solution saturated with the salt at 0° contains 132 g. per liter. It was also found that the sodium benzoyl peroxide could be thrown out of its saturated solution by salting out with sodium nitrate and also by the addition of alcohol. In this connection it was surmised that perhaps the presence of alcohol in the aqueous solution of the salt, when prepared by the method of Baeyer and Villiger, caused loss of active oxygen, but alcohol was found not to be oxidized by the salt in slightly alkaline solutions at 0°. Also the addition of alcohol to chloroform solutions of the free acid resulted in no reaction at 0°.

The chloroform solutions of benzoyl hydrogen peroxide, obtained by extracting the cold aqueous solutions, are slightly cloudy from moisture, but there is not sufficient moisture present to interfere with the preparation of the oxides from unsaturated hydrocarbons. Drying by calcium chloride in the cold does not cause loss of active oxygen.

Stability of Sodium Benzoyl Peroxide.—Two small flasks each containing 100 cc. of a saturated solution of the salt were surrounded with ice and connected with gas burets. To one flask 10 cc. of 20% caustic soda was added. At the end of two and one-half hours no oxygen had been evolved from either solution.

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