

were obtained. Several series of about twelve distillations each, using different amounts of acid, were conducted and the Duclaux constants for the three acids mentioned above were calculated. These constants varied somewhat from Duclaux's. The differences in the case of acetic acid are shown above.

Under the same experimental conditions and using these constants, accurate results were obtained with mixtures of two acids. The following example shows the nature of the results obtained with mixtures of two acids:

| | Acetic acid, g. | Propionic acid, g. |
|------------------------|-----------------|--------------------|
| Wt. of acid taken..... | 0.672 | 0.294 |
| Wt. of acid found..... | 0.674 | 0.300 |

In the judgment of the writer, it is impracticable to attempt to determine more than two or three acids in the same fraction. By proper fractional distillation the acids in the mixture may be quite well separated. This obviates the necessity of calculating as many as four acids from a single distillation, which is objected to by Upson, *et al.*

It is believed by the writer that the lack of agreement between different sets of Duclaux's constants, attributed by the authors just mentioned to unavoidable experimental variations, is due instead to impurities in the acids used and to avoidable experimental variations. The results obtained by the writer under closely regulated experimental conditions, are so concordant as to warrant much closer calculation of results than has been possible in the past, thus increasing the reliability of the method. Further difficulties suggested by the authors mentioned above might have been avoided by the use of qualitative tests to determine the presence or absence of certain acids and the relative claims to acceptance of two or more possible combinations.

In view of the publication of a new method for volatile fatty acids by steam distillation¹ which appears to have some advantages not possible of attainment by the Duclaux method, it seems inadvisable at present to continue further a study of the Duclaux method. However, in the opinion of the writer it is possible under proper conditions to obtain much more accurate results with the method than have generally been obtained.

AMES, IOWA.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF PRESIDENCY COLLEGE.]

NEUTRAL POTASSIUM PERSULFATE AS A REAGENT IN ORGANIC CHEMISTRY.

BY RASIK LAL DATTA AND JNANENDRA NATH SEN.

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The object of this investigation is to study the action of potassium persulfate on organic bodies in order to find out the many interesting

¹ Dyer, *J. Biol. Chem.*, 28, 445-473 (1917).

reactions produced by this compound. Its action on some of the aromatic hydrocarbons and acetic acid has been studied by Wollfenstein and his co-workers. The results obtained were quite interesting, and, in fact, the importance of these results led us to continue the investigation. They have shown in several communications¹ that aromatic hydrocarbons condense with the elimination of two atoms of hydrogen to form hydrocarbons of double molecular weight. For instance, dibenzyl is obtained from toluene; ethyl benzene gives dimethyldibenzyl. Similar results have been obtained with the xylenes, mesitylene and other substituted benzenes. They have also shown that acetic acid yields a small quantity of succinic acid.

The following results have been obtained: Hydroquinone, in the cold, is oxidized to a large degree to quinhydrone. Aniline gives a good yield of aniline black. *o*-Toluidine gives a theoretical yield of *o*-toluidine black. Acetanilide and benzanilide are oxidized to *p*-benzoquinone with the detachment of the acid radicles. Acetamide, propionamide and butyramide are hydrolyzed with the formation of the corresponding acids. Allyl alcohol is readily oxidized to acrolein.

In the case of benzamide, it was not hydrolyzed in the same way as the aliphatic amides but a complex acid was produced which is under investigation. Similarly, it was found that cinnamic acid, pinene, limonene gave yellow to brown products of high molecular weights. These are under investigation. With the aromatic amines and diamines, there were produced various dye-stuffs, which are, at present, under systematic examination.

The Preparation of Quinhydrone from Quinone.

Potassium persulfate gives a good yield of quinhydrone from hydroquinone. At first solutions of hydroquinone and potassium persulfate were mixed together and heated to boiling, but the result was a black mass. Repeated trials were made at different temperatures, but it was found that the ordinary temperature is best suited for the interaction between the substances. To an aqueous solution of hydroquinone a saturated solution of potassium persulfate was added, and in about half an hour beautiful, glistening crystals began to appear. Where the reaction was complete, they were filtered off, washed once or twice with cold water, and upon examination found to be quinhydrone, melting at 170°.

The best yield was obtained when the following proportions were used, and will serve as an elegant and economical method for the preparation of this compound: 5.32 g. of potassium persulfate were dissolved in 80 cc. water and to this 4.36 g. of hydroquinone dissolved in 4 cc. water were added gradually while shaking the mixture. In about a quarter of an hour, beautiful, glistening, green crystals began to separate. The

¹ *Ber.*, 32, 432, 2531; 37, 3221, 3225.

whole was left for half an hour and filtered. The solid was separated by suction and washed once or twice with distilled water. The yield obtained was 3.2 g., *i. e.*, 80% of the theory. As potassium persulfate is rather sparingly soluble, a large excess of water is involved and hence the yield could not be made greater on account of the slight solubility of quinhydrone itself. It should be noted also that quinhydrone is the only product in the cold even if a large excess of potassium persulfate be used.

Aniline.

Aniline was oxidized in the cold quantitatively to aniline black. Aniline was shaken with a saturated solution of potassium persulfate when it formed the following successive colorations: dirt color, red, brown, violet, and finally black. The whole was left for twenty-four hours in order to make sure that the reaction was complete. The product was washed with water and dried. The compound thus obtained was a black crystalline substance having a metallic lustre and was found to be pure aniline black. The yield obtained was quantitative.

Found: N, 15.28. Calc.: N, 15.38.

o-Toluidine.

About 10 cc. of freshly distilled *o*-toluidine are treated with a large excess of potassium persulfate solution and the whole shaken and allowed to stand for twenty-four hours at ordinary temperature. A black substance was found to be formed. This was filtered, well washed with water and afterwards with very dilute alcohol. The substance, on examination, was found to be pure *o*-toluidine black.

Found: N, 13.59. Calc.: N, 13.33.

Acetanilide.

A very concentrated solution of potassium persulfate was added to a small quantity of acetanilide and the mixture heated on the water bath. The whole turns red gradually. After about an hour the smell of quinone was noticed and at the same time a brown precipitate appeared. This was then extracted with ether. On evaporation of ether, yellow crystals were obtained, which melted at 116° and were identified to be quinone. It was to be noted that with free aniline no quinone was formed, but that in the case of its acetyl derivative, it was the main product.

Benzanilide.

When benzanilide was kept in contact with a strong solution of potassium persulfate in water at the ordinary temperature for about twenty-four hours, the solution was found to turn brown and a white solid separated. At the same time the odor of quinone was detected. This was filtered off and treated with alkali when it readily dissolved and was reprecipitated on the addition of dilute sulfuric acid. This was found to be

benzoic acid. The filtrate was extracted several times with ether. From the ether extract, golden-yellow crystals of quinone were obtained, melting at 116°. The yield of quinone was very small in this case.

Acetamide.

Persulfate solutions have a hydrolyzing action on acid amides. Acetamide was hydrolyzed when treated with a solution of potassium persulfate into acetic acid and ammonia. A quantity of acetamide was heated in a flask with a very concentrated solution of potassium persulfate for an hour on the water bath. At the end of the operation no acetamide could be detected, the solution containing ammonium acetate and free acetic acid.

Propionamide.

Propionamide, when similarly boiled with potassium persulfate, underwent hydrolysis and the resulting solution contained a mixture of propionic acid and ammonium propionate.

Butyramide.

Butyramide, on treatment with potassium persulfate, yielded a mixture of ammonium butyrate and butyric acid.

Allyl Alcohol.

Allyl alcohol yielded, on treatment with potassium persulfate, mainly acrolein, but at the same time a small quantity of some sticky substance was produced. Allyl alcohol was taken in a flask and to it a large excess of an almost saturated solution of potassium persulfate was added. The whole was kept at incipient boiling on water bath under reflux for nine hours. At the end of the reaction the solution left behind smelled strongly of acrolein. The solution was next extracted with ether, when all the acrolein with an oily viscous substance was extracted. On distillation of the ethereal solution the acrolein was found in the distillate and a viscous oily substance remained behind in the flask. This latter product is under investigation.

CALCUTTA.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF PRESIDENCY COLLEGE.]
**INDIRECT FORMATION OF DOUBLE SALTS VI: THE DOUBLE
SILVER, LEAD, BISMUTH, COPPER AND MERCUROUS
HALIDES OF SUBSTITUTED AMMONIUM BASES.**

BY RASIK LAL DATTA AND JNANENDRA NATH SEN.

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It has been shown in previous communications on the subject¹ that the indirect method of double salt formation is particularly suitable for the

¹ Datta, *J. Chem. Soc.*, 103, 426 (1913); Datta and Mukherjea, *Proc. Chem. Soc.*, 29, 185 (1913); Datta, *THIS JOURNAL*, 35, 949 (1913); Datta, *Ibid.*, 35, 1185 (1913); Datta and Ghosh, *Ibid.*, 36, 1017 (1914).