CHEMICAL SECTION.

Stated Meeting, held Thursday, October 15, 1903.

A Basic Reaction of Aromatic and Fatty Aldehydes.

BY SAMUEL S. SADTLER.

While carrying on some work in oils of orange and lemon, I found it very difficult to get accurate determinations of the citral in certain of these oils. They were so-called oleo-resins of orange and lemon, which contain a relatively large percentage of acid resins, and have not to my knowledge been, as yet, described. These oils are obtained by extraction with a volatile solvent, which seems to dissolve certain constituents from orange and lemon peel, which either are not extracted at all, or else in smaller proportion by the processes of expression. It is recorded as a fact that the gravity of machine-expressed oil is greater than hand-pressed, and these oils are heavier than either.

With the use of sodium bisulphite for determining the aldehydes the addition compound forms partly in the aqueous layer and partly in the oily layer, and further work is very discouraging when this stage is reached. I soon tried sulphite of soda instead of the bisulphite. On heating a solution of this with the oil, the dihydrodisulphonate of sodium is formed, which is soluble in water, and two molecules of sodium hydrate are split off. Tiemann, in his work on the aldehydes of lemon-grass oil, pointed out that the reaction could be indicated by phenolphthalein, and by adding a solution of sulphurous acid from time to time, the end of the reaction could be known and the difference of volume of the oil could be told. This, however, is not a method that is capable of the greatest accuracy, and requires a special form of flask.

It occurred to me that the alkali formed in this reaction might be titrated for with standard acid, omitting the bicarbonate of sodium used by Tiemann. I first tried this with a standardized solution of sulphurous acid, but later found

$N/2$ HCl, or normal HCl, very satisfactory and more convenient. It seems to require the use of more sulphite solution, however, as the sulphurous acid reforms sulphite from the NaOH split off. I will try, however, at a future time, to take up all the details necessary in the determination of citral as a matter by itself, and speak of the general procedure more especially at present.

From other tests on the oils in question, I found that they contained considerable quantities of acid resin, which would, unless previously neutralized, interfere with the results. In fact, I found the acid resin of the orange oil almost sufficient to neutralize all the alkali formed. This difficulty was overcome by neutralizing these acids first with dilute caustic potash solution ($N/2$ KOH being convenient for the purpose, and if done quantitatively, might be interesting as part of a more or less complete examination of the oil) and rosolic acid solution as indicator, which will serve as indicator in the subsequent reaction.

Analyses were made with oil of orange, but until the mixtures of aldehydes of this oil are more fully studied, I will not refer to figures obtained. If citral is not found to be the predominating aldehyde, the results would be of little value except as comparative.

For oil of lemon, 5 or 10 grams are weighed into an Erlenmeyer flask, and after neutralization, 25 or 50 cubic centimeters of a 20 per cent. sodium sulphite solution, depending upon the amount taken, is added. Before adding the sulphite solution, however, it is neutralized with a little $N/2$ HCl, after being heated by immersion in a water bath. The sulphite solution used in these experiments required about 75 cubic centimeters of $N/2$ HCl to neutralize at boiling temperature, with rosolic acid as an indicator. When the solutions were mixed a red color formed at once in the aqueous layer. This was discharged from time to time with $N/2$ HCl. The flask is then heated and agitated frequently. The reaction is complete in about half an hour, if kept hot, and the layers mixed frequently. When the color is all discharged, or all but a very faint pink, which is not appreciably affected by a few drops more of acid,

the number of cubic centimeters of standard acid is noted. An emulsion forms, due to the neutralized resins, but that does not interfere with the reaction, if care is exercised.

The reaction, as written by Tiemann, is:

and is probably correct, as the amount of citral and sulphite is shown below to be in the ratio of 1 to 2.

The amount of standard hydrochloric acid used expressed in terms of citral, in the above ratio of one molecule of citral to two molecules of HCl, divided by the weight of oil taken, gives the percentage of citral.

Analyses of citral in lemon oil, by this method, gave in two determinations:

	Per Cent.
I.	5'24
II.	5'29

I believe results within one or two tenths of a per cent. can be gotten in every case, with a little practice, by this method.

To check the accuracy of this reaction, I made some known mixtures of citral, which was kindly furnished by Dr. Harry F. Keller, and separated lemon-oil terpenes, previously freed from citral.

	Calculated.	Found.
I.	8'68	8'85
II.	12'11	12'15

The method was further checked by using some pure well crystallized vanillin (M. P., 81° C.). The phenolic hydroxyl of the vanillin was first neutralized with a little caustic potash solution until it became a faint pink, using a little rosolic acid, sulphite solution added and titrated hot with N/2HCl, having first neutralized the sulphite solution at water-bath temperature as in the case of citral.

	Calculated.	Found.
Vanillin	100'00	99'00

This was a rough check on the method, but as the vanillin had not been specially purified further examination

fact in regard to the growth of a piece of cast iron when heated repeatedly; then, so long as the heating will be repeated the growth or the expansion of the cubic contents of the piece of iron will continue? No! there must be a limit to the action of the gas, and that is when the cavities become too large and the pressure on the iron walls of the cavities must cease.

Yours respectfully,

E. GOLDSMITH.

658 N. TENTH STREET,

PHILADELPHIA, February 11, 1904.

Notes and Comments.

ELECTRIC RAILROAD CAR LIGHTING IN GERMANY.

As a result of many tests of various systems of railroad car lighting in Germany, the Prussian State Railway Administration has finally settled on a direct system of lighting from a single generator with a steam-driven dynamo, located on the locomotive, under the control of the engineer; also auxiliary or regulating storage batteries placed on each car of the train, thus rendering the lighting system on each car practically independent, its lights being assured a constant supply of current from its own accumulators, which accumulators are kept charged by the dynamo on the locomotive. It is stated that this combination meets more perfectly than any of the others the requirements of simple, economical and efficient construction, maintenance and attendance in regular service.—*Iron Age*.

ACETYLENE FROM CALCIUM CARBIDE.

A yield of 5 cubic feet of acetylene gas from every pound of calcium carbide is guaranteed by manufacturers in the United States. In Germany acetylene gas is mixed with a gas of lower candle-power, containing about 25 per cent. acetylene, and used in railroad cars.—*Engineering and Mining Journal*.

Franklin Institute.

[*Proceedings of the stated meeting held Wednesday, February 17, 1904.*]

HALL OF THE FRANKLIN INSTITUTE,
PHILADELPHIA, February 17, 1904

Vice-President JAMES M. DODGE in the chair.

Present, 106 members and visitors.

Additions to membership since last report, 16.

The following resolution was adopted with unanimity:

“*Resolved*, That the President and Secretary be directed to extend to our sister Society, the Maryland Institute for the Promotion of the Mechanic Arts,