tive index at different temperatures, has a large number of determinations of index of refraction at 15° C. and 60° C.

The following table of temperature corrections has been calculated by the writers from these results. Table IV shows remarkable agreement with Table III.

Oil.	Correction for 1° C. in refractive index.
Linseed	0.00037
Cotton	0.00037
Peanut	0.00037
Corn	0.00036
Sesame	0.00037
Olive	0.00037
Rape	0.00036

From these results it would seem that the correction for change in refractive index for the ordinary fats and oils is very uniform, about 0.000365 for 1° C.

THE PRODUCTION OF ACYLAMINES BY THE INTERACTION OF SODIUM SALTS OF MONOBASIC ACIDS AND AMINE HYDROCHLORIDES.

By Frederick L. Dunlap.

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During the course of some experimental work, I had occasion to try the action of sodium acetate on aniline hydrochloride. These two compounds reacted quite readily with the production of acetanilide. A brief study of this type of reaction was extended to analogously constituted bodies, the results of which experiments are given in this paper. This reaction was made use of with the sodium salts of acids containing both open and closed chains, and with alphyl- as well as with arylamines.

When the sodium salt of the monobasic aliphatic or aromatic acid is caused to react, under the influence of heat, the reaction proceeds as follows, R and R′ being either an alphyl or aryl residue:

$$RCOONa + R'NH_2HCl = R'NHCOR + NaCl + H_2O.$$

In two of the experiments, conditions were varied to see the effect of temperature and mass on the yield of the resulting product, namely, in the cases where calcium and sodium acetates reacted with aniline hydrochloride. In all other cases, reaction was brought about between molecular quantities. The calcium acetate mentioned above was the only salt other than a sodium salt made use of in this work.

No mention of such a reaction as has been outlined could be found in the literature; but after the experiments had been carried on for some time, it was found that this method had been the subject of the United States patent[1] for the manufacture of acetanilide from aniline hydrochloride and calcium or sodium acetate.

Inasmuch as this reaction took place so readily with the hydrochloride of the primary alkylamines, which we look upon as salts of substituted ammonia, there was every reason to expect that the reaction would also take place easily with ammonium chloride; and such was found to be the case, ammonium chloride reacting quite as readily as the alkylamine salts.

The reaction between the hydrochlorides of these primary alkylamines and the sodium salts of monobasic acids proceeds as follows: First, the splitting off of sodium chloride with the formation of free acid and free amine; second, the union of the amine and the acid; third, the breaking-down of the salt formed from the amine and the acid, under the influence of heat, to form the acylamine and water.

I. $RCOONa + R'NH_2HCl = NaCl + RCOOH + R'NH_2$.

II. $RCOOH + R'NH_2 = RCOONH_3R'$.

III. $RCOONH_3R' = RCONHR' + H_2O$.

In the cases where ammonium chloride was used, $R' = H$.

These stages are made sufficiently clear from the following facts: First, the formation of free acid is evidenced by the reaction resulting between sodium acetate and aniline hydrochloride, when these substances are ground together in a mortar, for a strong odor of acetic acid is developed. Then Lorin[2] has shown that when concentrated formic acid is heated in the presence of anhydrous sodium or potassium formate at 150°-155°, the formic acid decomposes into water and carbon monoxide. Formic acid alone decomposes at 160°, with the formation of hydrogen and carbon dioxide. When sodium formate and aniline hydrochloride were heated together in a sealed tube at 185°, no formamide was produced, but there was considerable gas pressure in the tube on

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[1] U. S. Patents 574,395 and 574,396.

[2] *Jahresbericht*, (1876), p. 515.

opening it, due to the formic acid produced by the reaction undergoing decomposition in one, or perhaps both, of the ways indicated.

Sodium formate itself does not undergo decomposition until it reaches a much higher temperature[1]. Second, if free acid is produced by such reactions, free amine must also be produced. The production of the latter was easily distinguished in some of the experiments. The production of a free acid, say acetic, and of a free amine, for example aniline, must result in the formation of a salt—in this case aniline acetate. Third, the production of acetanilide from aniline acetate by means of heat, is a well known reaction.

As has already been stated, but two series of experiments were conducted to see the effect of temperature and mass on the yield of the resulting product. In some of the results obtained, the yield must have been very largely influenced by the fact that the mixtures were charged into the sealing tubes in a perfectly dry condition, thus precluding any very intimate contact of reacting masses. The following list shows the mixtures that were used, and the resulting products:

	Product.
Sodium acetate and aniline hydrochloride·······	Acetanilide
Calcium acetate and aniline hydrochloride······	Acetanilide
Sodium acetate and *o*-toluidine hydrochloride···	*o*-Acettoluide.
Sodium acetate and ammonium chloride········	Acetamide.
Sodium benzoate and aniline hydrochloride·····	Benzanilide.
Sodium benzoate and ammonium chloride······	Benzamide.
Sodium benzoate and methylamine hydrochloride·	Methylbenzamide.
Sodium formate and aniline hydrochloride······	········

EXPERIMENTAL PART.

Sodium Acetate and Aniline Hydrochloride.—I. Molecular quantities of freshly fused sodium acetate and thoroughly dried aniline hydrochloride were heated, by means of an oil-bath, in a flask having a return condenser. The dry products were not intimately mixed before being introduced into the flask. Upon heating, the contents of the flask began to liquefy and turn dark. This mixture was heated for nearly three hours at 140°, and the acetanilide obtained amounted to 38 per cent. of the theoretical yield.

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[1] *Ber. d. chem. Ges.*, **15**, 1507 (1882).

II. This experiment was the same as the preceding one, except that the mixture was heated for seven and a half hours on a steam-bath. Yield of acetanilide, 23 per cent. of the theory.

III. Molecular quantities of sodium acetate and aniline hydrochloride were ground together in a mortar, in order to give an intimate mixture. In a few moments after the dry salts began to be triturated, the resulting product became pasty, and finally semi-fluid. This semi-fluid mass, which smelled strongly of acetic acid, was introduced into a sealing tube, and then heated for seven hours at 120°. After this treatment, the contents of the tube were purple in color, and there was no pressure on opening the tube. Yield, 54 per cent.

IV. This experiment was carried out similarly to the preceding one, except that twice the amount of sodium acetate was employed. This mixture was heated for three hours at 165°, and a yield of 71-72 per cent. was obtained.

V. Same as No. IV, except that the temperature was held at 120° for six hours. Yield, 65 per cent.

Calcium Acetate and Aniline Hydrochloride.—I. Molecular quantities, intimately mixed in a mortar, were heated in a sealed tube for five hours at 197°. Yield of acetanilide, 58 per cent.

II. Same as preceding experiment, except that the temperature of heating was 160°, while the duration of heating was but four hours. Yield, same as in No. I.

III. Where twice the amount of aniline hydrochloride was used, *i. e.*, theoretically enough of the hydrochloride to decompose the calcium acetate, and the mixture heated in a sealed tube for seven hours at 150°, the yield of acetanilide was nearly 50 per cent.

Sodium Acetate and o-Toluidine Hydrochloride.—Molecular quantities of these compounds were ground together in a mortar to mix them intimately. On grinding, this mass acted similarly to the sodium acetate and aniline hydrochloride mixture, *i. e.*, became at first moist and pasty, and finally semi-fluid. This mass was then charged into a sealing tube and heated for eight hours at 320°. There was no pressure on opening the tube. The tube was filled with a crystalline product which was purified by crystallization from benzene. The pure product melted at 109°. Alt[1] gives the melting-point of *o*-acettoluide as 110°, and

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[1] *Ann. Chem.* (Liebig), **252**, 319 (1889).

Wroblewsky[1] as 107°. From its physical and chemical properties, this body was easily recognized as *o*-acettoluide. Due to loss of mother-liquors, no yield was calculated.

Sodium Acetate and Ammonium Chloride.—Molecular quantities of these compounds were ground together as in the previous cases mentioned. During this process of grinding, the production of free ammonia was readily detected by its odor. This mixture was heated in a sealed tube for five hours at 240°. There was no pressure on opening the tube. The contents of the tube were partly liquid and partly solid; it was washed out with alcohol, the insoluble portion filtered off, and the alcoholic solution fractioned. A yield of about 40 per cent. of acetamide was obtained.

Sodium Benzoate and Aniline Hydrochloride.—Molecular quantities of these substances were intimately mixed in the usual manner. During the mixing the mass became damp, and the odor of free aniline was strongly developed. After heating in a sealed tube for four hours at 245°, the product was dark-colored, and the tube contained a crystalline product. After washing out the contents of the tube with cold water, then treating with dilute hydrochloric acid, the residue was treated with bone-black in an alcoholic solution and allowed to crystallize. When pure, the product melted at 160°; it was easily identified as benzanilide. Yield, 30 per cent.

Sodium Benzoate and Ammonium Chloride.—Molecular quantities, after mixing, were heated for eight hours at 260°. The contents of the tube were washed thoroughly with small quantities of cold water, then recrystallized from boiling water. This product by repeated crystallization could not have its melting-point raised beyond 125°. The melting-point of benzamide is usually given as 128°; for example, it is so given in Gattermann's "Praxis des organischen Chemikers". A sample of Kahlbaum's benzamide melted at 125°, and repeated crystallization would not raise it higher.

Apropos of the question of the discrepancy in the melting-point of benzamide, it is of interest to note the effect on the melting-point by the use of the two types of melting-point apparatus usually employed in these determinations. These two types, which are fully described in Gattermann's "Praxis des organischen Chemikers," differ essentially in the fact that the first has a greater

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[1] *Ann Chem.* (Liebig), **168**, 162 (1873).

or less portion of the thermometer enclosed by a glass tube, the liquid in which the thermometer bulb is placed being heated with a free flame. In the second type, moreover, the thermometer stem is exposed directly to the air, the small beaker in which the bulb is placed being separated from the flame by wire gauze. In the first type heat is conveyed through the liquid by the convection currents; in the second, convection currents are done away with, as far as possible, by constant agitation with a hand stirrer.

In the first type mentioned (a 250° milk glass thermometer being used) benzamide melts from three-quarters to one degree higher than when the determination is made with the second type. The higher the melting-point, the greater will be the discrepancy in the readings between these two types. The higher reading in the first method is easily accounted for by the fact that the temperature of the air between the glass envelope and the thermometer is at a higher temperature than the air surrounding the thermometer stem in the second type. This must result in a higher reading, and one that is therefore nearer to the corrected melting-point. The melting-points given in this paper were made according to the second method.

Sodium Benzoate and Methylamine Hydrochloride.—When molecular quantities of these substances were ground together, the odor of methylamine was developed. The mixture was heated in a sealed tube for twelve hours at 280°, and on opening the tube, while there was no pressure, there was a slight odor of methylamine. The tube was filled with a pale yellow viscous liquid and some crystals. On shaking up the contents of the tube with cold water, this yellow liquid solidified. It was filtered, dried, dissolved in ether, and precipitated out with low boiling ligroïn. This method of purification is much preferable to the one given by van Romburgh,[1] who purified methylbenzamide by crystallizing from hot water. The yield of methylbenzamide obtained was 32 per cent. of the theory and it had a melting-point of 78°.

Sodium Formate and Aniline Hydrochloride.—When these compounds, intimately mixed, were heated in a sealed tube to 185° for seven hours and then cooled, the tube, on opening, exhibited considerable gas pressure and was filled with a dark liquid (aniline). From the contents of the tube no formamide was obtained.

CHEMICAL LABORATORY,
UNIVERSITY OF MICHIGAN.

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[1] *Rec. trav. chim. Pays-Bas*, 4, 388 (1885).