Cotton cellulose is fundamentally different from the cellulose in wood; this is brought out by the adsorption curves not coinciding over any portion of their length.

A hysteresis effect between gain and loss of water has been found, except at low vapor pressures, but the higher value attained by the loss of water is considered to represent the true equilibrium value at any vapor pressure.

By an application of modern gel theory a theoretical explanation of the observed facts is offered.

MONTREAL, CANADA

[CONTRIBUTION FROM THE KENT CHEMICAL LABORATORY OF THE UNIVERSITY OF CHICAGO]

SALTS OF NITRILES. III. SODIUM PHENYLACETONITRILE[1]

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In 1927 and 1928 Rising and Zee reported the preparation, isolation and properties of the sodium salt of phenylacetonitrile, $[C_6H_5CHCN]Na$, and of α-phenylbutyronitrile,[2] $[C_6H_5C(C_2H_5)CN]Na$. Early in 1929 a further paper was published by Rising, Muskat and Lowe on the potassium salt of phenylacetonitrile.[3] In these papers certain conclusions are stated, based upon the behavior of the salts. (1) The salts exhibit tautomerism of the carbide–nitride type, analogous to the well-known tautomerism of the salts of acetoacetic ester

$$[C_6H_5CH{=}C{=}N^-]Na^+ \rightleftharpoons [C_6H_5C^-HCN]Na^+ \qquad (1)$$
$$[C_6H_5C(C_2H_5){=}C{=}N^-]Na^+ \rightleftharpoons [C_6H_5C^-(C_2H_5)CN]Na^+ \qquad (2)$$

(2) Each salt reacts in a nitride form. The evidence for this conclusion is presented in the papers named. (3) Each salt reacts also in a carbide form. The evidence for this conclusion is presented in the papers mentioned.

Because of the difficulties met by a number of workers who have tried to repeat Zee's work,[4] a thorough reinvestigation of the problem was undertaken by the present authors.[5] Sodium phenylacetonitrile was

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[1] The work here reported was completed by April 15, 1929, but publication was postponed out of courtesy to Professor F. W. Upson and his collaborators until they should have reported upon their recently resumed work on the same problem, upon which they have published nothing since 1922 [Upson and Thompson, THIS JOURNAL, **44,** 181 (1922)]. See also THIS JOURNAL, 51, 263 (1929). These authors have just announced by an abstract a paper on the subject to be presented at the Minneapolis meeting of the Society and we feel free, therefore, to report our findings.

[2] Rising and Zee, (a) *ibid.*, **49,** 541 (1927); (b) **50,** 1699 (1928).

[3] Rising, Muskat and Lowe, *ibid.*, **51,** 262 (1929).

[4] See footnote, Ref. 2b, p. 1699.

[5] I wish to express here my sincere appreciation of the fine technique of my collaborator, Dr. Géza Braun, International Research Fellow of Budapest, at the University of Chicago, 1926–1928. M. M. RISING.

first studied, as pure phenylacetonitrile is readily obtained. A summary of the work of the present authors is as follows.

(1) Phenylacetonitrile of freezing point −24° was used, its purity being further checked by its refractive index.

(2) An apparatus (diagram) was devised for the preparation of sodium phenylacetonitrile in an atmosphere of nitrogen. It is extremely important to protect the salt from air and moisture, since it is quickly decomposed by exposure to either. When brought into contact with air the salt smokes, glows and turns to a tar which slowly hardens.

(3) Sodium phenylacetonitrile was prepared by treatment of phenylacetonitrile with powdered sodium in dry ether, the reaction being carried out in an atmosphere of nitrogen. The salt was precipitated from its ethereal solution by means of ligroin, the operation being performed with complete exclusion of air. Analysis of the salt (which was always handled under ligroin or in an atmosphere of nitrogen) showed it to contain 15.79 and 15.76% of sodium (calcd., 16.53).

(4) Sodium phenylacetonitrile was found to be very soluble in ether. When prepared as just described it remains in solution in the reaction mixture, whereas the sodium cyanide formed as a by-product of the reaction (Equation 5) is precipitated and can be removed by filtration. The behavior of the salt was studied in ether solution and a number of observations were made.

(a) Cooling of the ether solution of the salt to −80° causes the salt to separate in fine large crystals. When the ethereal solution is stirred vigorously at −80°, a mass of finer crystals separates. The solid salt was not isolated under these conditions since it redissolves readily in the ether as the mixture warms up.

(b) Acidification of an ether (or aqueous) solution of the salt yielded pure phenylacetonitrile in nearly quantitative amount. No hydrocyanic acid was liberated in the treatment with acid.

$$2[C_6H_5CHCN]Na + H_2SO_4 \longrightarrow Na_2SO_4 + 2C_6H_5CH_2CN \qquad (3)$$

(c) Treatment of the ethereal solution of the salt with ethyl iodide produced α-phenylbutyronitrile in excellent yield.

$$[C_6H_5CHCN]Na + C_2H_5I \longrightarrow C_6H_5C(C_2H_5)HCN + NaI \qquad (4)$$

(5) Sodium phenylacetonitrile is fairly stable in ether solution but it undergoes a change during and following its precipitation by ligroin. The ethereal solution does not contain even a trace of sodium cyanide, but after the salt is precipitated with ligroin it gives a test for cyanide and cannot be redissolved completely in ether; nor could perfectly pure phenylacetonitrile be recovered from the precipitated salt by treatment with acid, and a low yield was obtained from it by ethylation, all in marked contrast to the behavior of the salt in ethereal solution before precipita-

tion, which has just been described. Evidently the salt is far less stable in its solid form than in solution.

(6) The reaction of phenylacetonitrile with sodium was studied quantitatively to determine the exact course of the reaction and the amount of each product formed. The details and results of this study are to be found in the Experimental Part of this paper. It is there shown that the course of the reaction of phenylacetonitrile with sodium may be summarized in the equation

$$2C_6H_5CH_2CN + 2Na \longrightarrow [C_6H_5CHCN]Na + NaCN + C_6H_5CH_3 \qquad (5)$$

It has been proved by us further that the formation of sodium cyanide and toluene results from the reduction of part (about one-half) of the sodium phenylacetonitrile by the hydrogen liberated in the action of sodium on phenylacetonitrile according to the equations

$$2C_6H_5CH_2CN + 2Na \longrightarrow 2[C_6H_5CHCN]Na + 2H \qquad (6)$$
$$[C_6H_5CHCN]Na + 2H \longrightarrow C_6H_5CH_3 + NaCN \qquad (7)$$

This result agrees with the observations of E. von Meyer and his collaborators.[6] However, these earlier investigators obtained a salt of formula $C_{16}H_{13}N_2Na$, the salt of a condensation product rather than of the nitrile itself. Condensations (of the aldol type) probably occur in this series, exactly as in the formation of acetoacetic ester from ethyl acetate. The formation of hydrogen as a by-product of the reaction, as expressed in Equation 6, and the consequent partial reduction of sodium phenylacetonitrile to toluene and sodium cyanide (Equation 7) is highly undesirable from the point of view of yield of the salt. Since this salt and others of its kind are exceedingly important compounds, not only for their theoretical interest but as preparative reagents, it is of vital importance to develop methods of preparation in which the yield of the salts is not diminished by their reduction. Methods of this sort have been studied by Rising and collaborators,[7] in which sodamide and sodium ethylate are used to produce the salts rather than metallic sodium. Success has attended these efforts and excellent yields of the pure salts have been obtained in the case of a number of nitriles. These results will be published in due time.

Experimental Part

The Course of the Reaction of Sodium with Phenylacetonitrile. The Isolation of Pure Sodium Phenylacetonitrile, $[C_6H_5CH{=}C{=}N^-]Na^+$ and $[C_6H_5C^-HCN]Na^+$.

1. **Apparatus and Reagents.**—Reactions were carried out in Apparatus I (diagram). Apparatus II consists of Apparatus I to which an apparatus for filtration in an atmosphere of nitrogen is added. Before use all apparatus was freed from air and moisture by passage through it of a stream of dry oxygen-free nitrogen for two hours, while Flask A was warmed. All reactions were carried out in an atmosphere of pure nitrogen.

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[6] Wache, *J. prakt. Chem.*, **39**, 245 (1889); von Meyer, *ibid.*, **52**, 114 (1895), etc.

[7] Work on these problems is being continued by M. M. Rising with the coöperation of E. W. Lowe, C. M. Marberg and K. T. Swartz.

Eastman's best phenylacetonitrile was used, after two fractionations, the product showing a freezing point of −24° and n_D^{20} 1.5242.

2. **Procedure. Preparation of the Salt.**—When Apparatus I is ready for use, freshly cut sodium (13.0 g.), used in 15% of the calculated amount (Equation 7), is introduced into Flask A under dry xylene and powdered in the usual way. The xylene is then replaced by 250 cc. of ether, and nitrogen is led through the apparatus for three hours. The ether is then boiled for fifteen minutes and phenylacetonitrile (58.5 g.), in a 50% ethereal solution, is added from the dropping funnel during forty-five minutes, the reaction mixture being kept boiling and being vigorously stirred. The sodium dissolves, a precipitate appears and the solution becomes yellow. After the addition of the nitrile the reaction mixture is boiled for two hours, and the reaction is then complete. During the entire operation and during the filtration of the solution, nitrogen is led through the apparatus. Stirring can be carried out in such a way that the unused sodium collects in a mass.

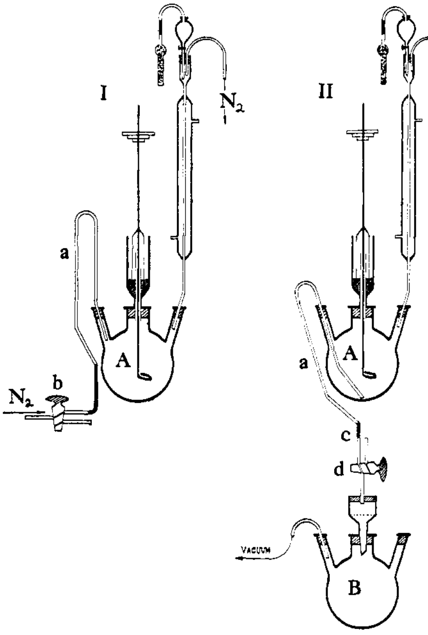

Fig. 1.

Filtration.—When the reaction just described is complete, the precipitate is allowed to settle. Siphon a is now attached by means of the rubber connection on Tube c to Flask B, which carries a filter funnel closed with a rubber stopper. This stopper holds a three-way stopcock, d. The direction of the nitrogen stream is now reversed, so that the gas enters the apparatus at the top of the condenser and leaves through a side arm of Flask B. The apparatus is evacuated, Siphon a is lowered into the clear solution in Flask A and filtration is started by opening Stopcock d. When the supernatant liquid is removed, Siphon a is lowered to the bottom of Flask A; the precipitate is drawn upon the filter and washed with ether introduced through the dropping funnel. The unused sodium remains in Flask A, the precipitate on the filter is sodium cyanide, and Filtrate F contains sodium phenylacetonitrile and toluene.

3. **Quantitative Determination of the Course of the Reaction.**—This was accomplished by determining (1) the amount of sodium left unused, (2) the amount of sodium cyanide formed and (3) the amount of sodium phenylacetonitrile produced.

(1) **Unused Sodium.**—The 15% excess of sodium, used to bring the reaction to completion, remained in Flask A. It was dissolved in alcohol and the alcoholic solution titrated in the usual way. In four preparations of the salt, in each of which 13.0 g. of sodium and 58.5 g. of nitrile were used, 1.4 g. of sodium remained unused (Equation 5). The theoretical amount of sodium was therefore consumed in the reaction.

(2) **Sodium Cyanide.**—The light colored precipitate formed in the reaction mixture, in quantity 13–14 g., proved to be nearly pure sodium cyanide.

Anal. Subs., 0.4100, 0.3322 (from two different preparations): Na_2SO_4, 0.5449, 0.4755. Calcd. for NaCN: Na, 46.97. Found: Na, 43.00, 41.50.

The amount of sodium cyanide so obtained in a given preparation was determined by titration with silver nitrate. From 13.09 g. of sodium and 58.5 g. of nitrile, 11.7 g. of sodium cyanide was produced, corresponding to 5.49 g. of sodium, and to 95.3% of the amount of cyanide which could be formed from phenylacetonitrile and sodium (Equation 5). In similar experiments an average of 11.88 g. of cyanide was formed, corresponding to 50% of the nitrile used.

(3) **Sodium Phenylacetonitrile.**—Filtrate F was investigated (a) to determine the amount of sodium phenylacetonitrile formed and so account for the rest of the sodium used and (b) to isolate the salt for analysis.

(a) **Quantitative Determination of the Salt.**—This was accomplished in two ways: by ethylation of the salt in Filtrate F, a nearly quantitative yield of α-phenylbutyronitrile being so obtained, and by conversion of the salt into phenylacetonitrile in nearly quantitative yield by treatment with acid.

Ethylation.—For the ethylation of the salt, Flask B, containing Filtrate F, was put in place of Flask A and 50 g. of ethyl iodide was introduced with vigorous stirring during twenty minutes (nitrogen atmosphere). The reaction mixture was then heated for an hour and to it was added ligroin (b. p. 30–50°) to precipitate the sodium iodide formed in the alkylation. The iodide was collected and its purity determined by titration with silver nitrate. The total amount of iodide produced was found to be 34.8 g., corresponding to 5.34 g. of sodium. The α-phenylbutyronitrile was separated from the reaction mixture by fractional distillation. Fraction I boiled up to 110° at 15 mm., weighed 9 g. and had the odor of toluene. Of this 4 g. boiled at 105–108° and 4 g. at 108–110° at atmospheric pressure, the fraction of b. p. 108–110° showing n_D^{20} 1.4960 (pure toluene n_D^{20} 1.49552). The residue from the crude toluene boiled at 122° at 15 mm., the distillate showing n_D^{20} 1.5097 (pure α-phenylbutyronitrile n_D^{20} 1.5092). The amount obtained was 31.7 g., a 94% yield of the nitrile calculated on the basis of the sodium in the ethereal solution (5.34 g. of sodium in the sodium iodide formed).

The quantitative study of the reaction has shown that of the 13.0 g. of sodium used to react with 58.5 g. of nitrile, 5.34 g. was converted into sodium phenylacetonitrile, 5.49 g. into sodium cyanide and 1.4 g. was unused. We have therefore accounted for 12.32 g. of the sodium used, or 95% (5% loss in operations, etc.).

(b) **Treatment of Sodium Phenylacetonitrile with Acid.**—A filtrate, F, containing the salt obtained by treatment of 58.5 g. of phenylacetonitrile with 13.0 g. of sodium, was treated with a small excess over the calculated amount of dilute sulfuric acid, while being stirred and kept cold. The ether layer which separated was removed, washed and dried. After evaporation of the ether, a residue of oil yielded on distillation under reduced pressure a fraction boiling up to 110° at 16 mm. This distillate weighed 8.0 g. and contained toluene. The main fraction of distillate, 25.2 g., boiled at 112–113° at 16 mm. and showed n_D^{20} 1.5242 (pure phenylacetonitrile n_D^{20} 1.5242).

4. **Reduction of Sodium Phenylacetonitrile by Hydrogen.**—A filtrate, F, obtained from 58.5 g. of nitrile and 13.0 g. of sodium in the way described, was refluxed for three hours with 13.0 g. of sodium powder and 75 cc. of absolute alcohol, the mixture being stirred. After removal of excess sodium, the reaction mass was dissolved in water and this solution was extracted with ether. When the ether extract had been dried and the ether removed, the oil which remained yielded on distillation 10 g. of pure toluene, n_D^{20} 1.4958 (pure toluene n_D^{20} 1.49552). The aqueous solution was found by the Volhard method to contain 8.2 g. of sodium cyanide, or 75% of the amount obtainable according to Equation 7.

5. **Isolation of Sodium Phenylacetonitrile.**—The reaction mixture obtained by treatment of 25.0 g. of phenylacetonitrile with 5.05 g. of sodium in the way described was filtered into 1.8 liters of ligroin (b. p. 30–50°) in a stream of nitrogen. A light yellow

salt precipitated in large quantity. A suspension of the salt in ligroin was transferred to a weighed flask and the ligroin was removed at reduced pressure in a nitrogen atmosphere. Sodium phenylacetonitrile remained in the weighing bottle.

Anal. Subs., 0.4706, 0.6150 (from two different preparations):[8] Na_2SO_4, 0.2295, 0.2995. Calcd. for NaC_8H_6N: Na, 16.53. Found: Na, 15.79, 15.76.

Properties of Sodium Phenylacetonitrile. 1. **Physical.**—The salt is a light yellow amorphous powder as precipitated from ether by ligroin at room temperature. A 10% ether solution of the salt cooled to $-80°$ slowly deposits large crystals. The salt is very soluble in ether and in phenylacetonitrile; it is insoluble in ligroin.

2. **Chemical.**—The salt turns brown immediately upon exposure to air, then smokes, collapses, glows and turns to a tar which hardens on cooling. The products of this decomposition are being studied. When the salt is precipitated with ligroin, a slow decomposition into sodium cyanide occurs. Not all of the salt so precipitated can be redissolved in ether and the insoluble residue contains sodium cyanide. The same change occurs after redissolving and reprecipitating the salt. Treatment of the salt with acid converts it into phenylacetonitrile. Reduction of sodium phenylacetonitrile with hydrogen was found to produce toluene and sodium cyanide. Hence it is to be concluded that the hydrogen formed when phenylacetonitrile is treated with sodium (Equation 6) reduces part of the sodium salt, under the conditions used by Braun (and von Meyer).

Summary

1. The von Meyer reaction of phenylacetonitrile with sodium has been studied quantitatively and the exact course of the reaction established.
2. A satisfactory method for the preparation and isolation of pure sodium phenylacetonitrile has been developed and used with excellent results by a number of workers.
3. The reducing action of hydrogen formed in the reaction of sodium with phenylacetonitrile has been found to account for the failure to obtain sodium phenylacetonitrile in quantitative yield.

CHICAGO, ILLINOIS

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[8] The first of the two sets of data was obtained by C. M. Marberg, who prepared the salt by the Braun method.