yield.[1] Under the same conditions of hydrolysis the N-alkyl-N′-nitroguanidines yield nitrous oxide, the alkylamine, and guanidine carbonate; small quantities of alkylguanidine also have been isolated.[2] In connection with some other work, the hydrolysis of nitroaminoguanidine[3] in a solution of ammonium carbonate was investigated and found to be analogous to these other reactions. The following products were isolated and identified: hydrazine, guanidine, nitroguanidine, aminoguanidine and diaminoguanidine. The dearrangement mechanism for nitroguanidine derivatives, as proposed by Davis and co-workers,[1,2] satisfactorily accounts for the formation of these compounds

$$\mathrm{NH_2NHC(NH)NHNO_2}\left\{\begin{array}{ll} \rightleftarrows \mathrm{NH_2NH_2 + N{\equiv}C{-}NHNO_2} & (1) \\ \rightleftarrows \mathrm{NH_2NO_2 + N{\equiv}C{-}NHNH_2} & \\ \qquad\qquad \downarrow & \\ \qquad\qquad \mathrm{N_2O + H_2O} & (2) \end{array}\right.$$

$$\mathrm{N{\equiv}CNHNO_2 + NH_3 \rightleftarrows NH_2C(NH)NHNO_2} \quad (3)$$

$$\mathrm{N{\equiv}CNHNH_2 + NH_3 \rightleftarrows NH_2C(NH)NHNH_2} \quad (4)$$

$$\mathrm{N{\equiv}CNHNH_2 + NH_2NH_2 \rightleftarrows NH_2NHC(NH)NHNH_2} \quad (5)$$

$$\begin{array}{l} \mathrm{NH_2{-}C(NH)NHNO_2 \rightleftarrows N{\equiv}C{-}NH_2 + NH_2NO_2} \\ \qquad\qquad\qquad\qquad\qquad\qquad\quad \downarrow \\ \qquad\qquad\qquad\qquad\qquad\qquad \mathrm{N_2O + H_2O} \quad (6) \end{array}$$

$$\mathrm{N{\equiv}C{-}NH_2 + NH_3 \rightleftarrows NH_2C(NH)NH_2} \quad (7)$$

Experimental

Twelve grams of nitroaminoguanidine (96% purity), 15.1 g. of ammonium carbonate, and 50 ml. of water were heated at 60–65° for twenty-five minutes. Gas was evolved vigorously and the solution developed an orange-red color. The reaction was completed by raising and holding the temperature at 75–80° for ten minutes. After adding 25 ml. of water, the solution was cooled to 30°, acidified with concentrated nitric acid, and finally chilled overnight at 0°. The white, fluffy solid (A) was recovered by filtration and washed with two 15-ml. portions of ice-cold water. The yield of dried product amounted to 2.4 g.; m. p. 170–185° (dec.). The filtrate and washings were combined and saved (B).

I. **Separation and Identification of Nitroguanidine and Nitroaminoguanidine in Fraction (A).**—The crude solid material was dissolved in 75 ml. of boiling water containing 1.0 ml. of glacial acetic acid. One ml. of benzaldehyde was added with stirring. A white precipitate formed immediately and was removed by filtration from the hot solution. The yield was 0.3 g.; m. p. 180–181°. Recrystallization from 95% ethyl alcohol gave hair-like needles, m. p. 185–186°; a mixed m. p. with the nitroguanyl hydrazone of benzaldehyde[4] was the same. From the filtrate, there was recovered after evaporation and cooling, 1.7–1.8 g. of material melting with decomposition at 232–235°. A mixed m. p. with nitroguanidine was 235–236°; an X-ray powder pattern on this material was identical with that obtained on a known specimen of nitroguanidine. The recovery corresponded to an 18–19% conversion to nitroguanidine.

II. **Isolation and Identification of Hydrazine, Aminoguanidine, and Diaminoguanidine in Filtrate (B).**—The filtrate and washings were heated to 60° and shaken for fifteen minutes with 15 ml. of benzaldehyde. After the solution remained at 0° for several hours, the precipitate was removed by filtration. The filtrate again was retained (C). The yield of dry hydrazones was 19.9 g. By extraction with four 50-ml. portions of boiling petroleum ether (b. p. 65–75°), 5.2 g. of crude benzalazine, m. p. 70–75°, was recovered. Recrystallization from either petroleum ether or ethyl alcohol raised the m. p. to 92–93°; a mixed m. p. with an authentic sample of benzalazine was the same. The yield of crude azine corresponded to a 27% conversion of the nitroaminoguanidine to free hydrazine.

The benzalazine-free hydrazones were extracted next with one 1500-ml. portion and four 200-ml. portions of boiling water. There was 0.5 g. of insoluble residue; m. p. 182–183°; a mixed m. p. with the nitroguanyl hydrazone of benzaldehyde was 183°.

The aqueous extract was cooled slowly to room temperature and the solid material removed. The yield of dried product was 5.2 g.; m. p. 154–156°. Several attempts to purify this fraction as the nitrate salt were unsuccessful. However, when it was converted into the free base and recrystallized from ethyl alcohol, yellow plates and needles, melting sharply at 180–181°, were obtained. A mixed m. p. with a known sample of dibenzaldiaminoguanidine was 181°; with benzalaminoguanidine, 153–157°. This crude nitrate also gave a sparingly soluble picrate from hot 95% ethyl alcohol, that melted at 242° without further purification; a mixed melting point with a pure specimen of dibenzaldiaminoguanidine picrate was 242–243°. The yield of diaminoguanidine was approximately 17%.

The 2300 ml. of mother liquor left after removing the dibenzaldiaminoguanidine nitrate were evaporated to 250 ml. and cooled for several days at 0°. Ultimately, 6.7 g. of crude benzalaminoguanidine nitrate (32% yield) were recovered; m. p. 155°. After repeated recrystallizations from water, the product melted at 167°; a mixed m. p. with benzalaminoguanidine nitrate was 170–171°. The picrate from alcohol decomposed at 253–254°; a mixed melting point with a known specimen was not depressed.

III. **Isolation of Guanidine in Filtrate (C).**—The aqueous filtrate from which the hydrazones had been separated was evaporated to dryness on the water-bath. By fractionally crystallizing this residue from 95% ethyl alcohol, most of the ammonium nitrate was separated from the small quantity of guanidine nitrate that remained in the last mother liquor. Final isolation of the guanidine as a reasonably pure derivative was made by preparing and fractionating the picrates from ethyl alcohol. The yield was 0.5 g.; m. p. 314–318° with decomposition (Davis[5] reports a melting point of 318.5–319.5° for guanidine picrate).

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[1] Davis and Abrams, *Proc. Am. Acad. Arts and Sciences*, **61**, 437 (1926).

[2] Davis and Elderfield, This Journal, **55**, 731 (1933).

[3] Phillips and Williams, *ibid.*, **20**, 2465 (1928).

[4] Whitmore, Revukas and Smith, *ibid.*, **57**, 706 (1935).

[5] Davis, "Chemistry of Powder and Explosives," John Wiley & Sons, Inc., New York, N. Y., 1943, p. 168.

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Small-Angle Scattering of X-Rays and the Micellar Structure in Cellulose Fibers

By A. N. J. Heyn

In a previous communication[1] it was shown that different cellulose fibers produce different

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[1] A. N. J. Heyn, This Journal, **70**, 3138 (1948); comp. also *Text. Res. J.*, **19**, 163 (1949).

small-angle scattering diagrams. If the crystalline domains are oriented parallel to the fiber axis, the scattered intensity extends exclusively along the equator; however, if the axis of crystallites forms an angle with the fiber axis the pattern consists of two oblique lines, the angle between which equals twice the angle between fiber axis and crystallites. The latter fact suggests that the phenomenon is a consequence of an internal diffraction of the X-rays rather than a surface effect.

The different angular intensity distribution of the small-angle scattering in various fibers is ascribed to different micellar distances assuming that Kratky's evaluation[2] of this effect is correct and that the scattering elements can be identified with the crystalline domaines or micelles.

This note offers a direct experimental proof that there exists a close relationship between the intermicellar distances and the intensity distribution in the small angle pattern by studying the result of changes of the intermicellar distances on the small angle pattern. Any treatment which increased the intermicellar dimensions reduced the length of the small-angle scattering as should be expected from Bragg's law and any decrease of the distance between the crystallites increased this length.

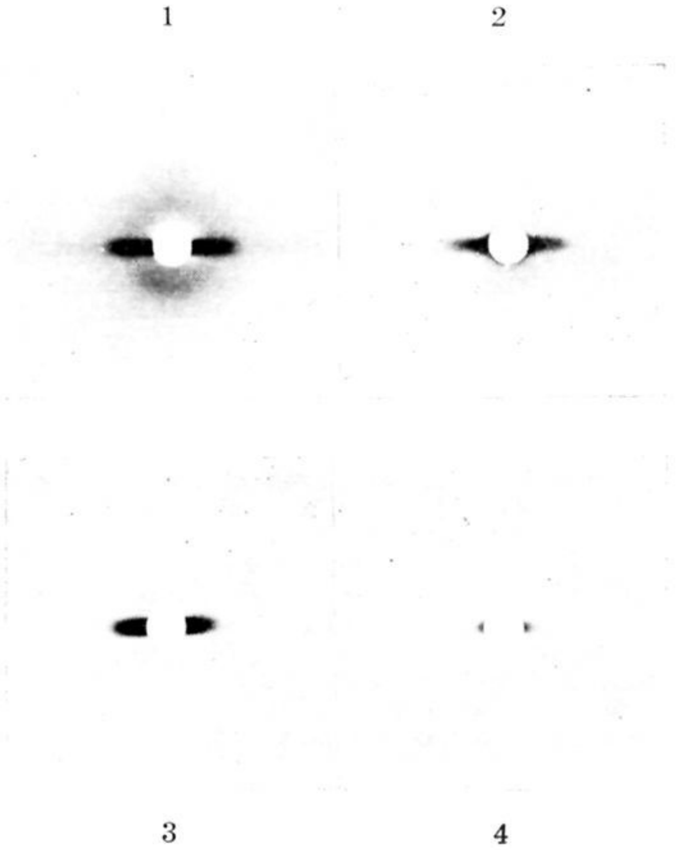

Fig. 1.—The influence of swelling in liquids and the deposition of crystals in the intermicellar spaces on small-angle scattering in a cellulose fiber; (1) scattering by untreated fiber in dry state; (2) pattern produced by fiber after deposition of gold crystals in the intermicellar spaces almost a similar pattern is obtained after deposition of sodium chloride or dry saccharose crystals; (3) pattern produced by fiber swollen in 0.5 % potassium hydroxide—Almost a similar pattern is obtained after swelling in cuprammonium; (4) pattern produced by fiber swollen and mercerized in 18 % potassium hydroxide. The pattern of the controls for (3) and (4) were similar to (1).

The following experiments illustrate this:

(A) **Swelling in Water.**—After swelling the cellulose fiber in water the resulting pattern lines show a slight decrease in length with a corresponding increase of intensity and broadening of width. The shortening of the pattern lines is in accordance with the increased micellar distance after swelling; while the greater intensity may be ascribed to the return of the crystallites from a probable distorted arrangement in the dry state to a more regular distribution in the wet state (the latter state, after all being the initial one of natural fibers). Upon redrying the sample the original pattern was obtained.

(B) **Swelling in Potassium Hydroxide.**—When the fiber was subjected to progressively increasing concentrations the pattern obtained was characterized by an ever decreasing length of the scattering lines (compare parts 1, 3 and 4 of Fig. 1). Whereas the change produced by low concentrations was reversible after washing in water and drying, high concentrations that completely mercerized the material produced a permanent shortening of the pattern lines.

(C) **Swelling in Cuprammonium.**—A change in length of the scattering line was found to be similar in nature to the change caused by swelling in water, the only difference being that the line was shorter in this case which is in accordance with the greater swelling in cuprammonium.

(D) **Depositing Various Crystallites in the Intermicellar Spaces.**—Deposition of gold crystals in the intermicellar spaces by soaking the fiber in gold chloride solution and subsequent irradiation resulted in a shortening and decreasing width of the scattering lines (compare parts 1 and 2 of Fig. 1). This may be partly due to the forcing apart of the micelles by the gold crystals and partly by the disarrangement of the micelles by the irregularly distributed gold crystals. Soaking of the fiber in a concentrated sodium chloride solution followed by drying resulted in a similar change of the scattering pattern. Washing in water of the so treated fiber for only one-fourth of a minute and drying restored the pattern to its original size and form. The washing either partially or totally dissolved the salt crystals, therefore allowing the micelles to resume their original position. The same scattering pattern was obtained using saccharose in place of salt which eliminates the possibility of a direct interference by metallic ions (as used in the two previous methods) with X-ray radiation causing the observed scattering change.

The above experimental proofs of the relation between micellar distance and X-ray scattering allows another important conclusion. As the

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(2) O. Kratky, *Naturwiss.*, **26**, 94 (1938); **30**, 542 (1942); O. Kratky, A. Sekora and R. Treer, *Z. Elektrochem.*, **48**, 587 (1942); O. Kratky and Wurster, *ibid.*, **50**, 249 (1944).

distance and regularity in distribution of the micelles, rather than their size (which remains unchanged in most of the above experiments), determines the scattering it follows that, to a high degree, phase relationship between the micelles is involved in the scattering by these densely packed cellulose systems. Such a phase relationship will not exist in the scattering by particles in more dispersed systems. In the latter case formulas given by Guiniér and others[3] are appropriate and enable the determination of the *size* of the particles; whereas the application of Bragg's law appears to be applicable in this densely packed system enabling calculation of the average *distance* between the particles.

(3) A. Guiniér, "Radiocrystallographie," Chapter XII, Dunod, Paris; *C. R. Acad. Sci.* Paris, **204**, 1115 (1937); Thesis, Paris, 1939; R. Hosemann, *Z. Physik*, **113**, 751 (1939); **114**, 133 (1939); O. Kratky, *J. Polymer Sci.*, **3**, 195 (1948).

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Synthesis of N^1-*p*-Fluorophenyl-N^5-isopropyldiguanide[1]

BY CHARLOTTE A. HART AND CALVIN A. VANDERWERF

In connection with an investigation of the pharmaceutical properties of aromatic fluorine-containing compounds, N^1-*p*-fluorophenyl-N^5-isopropyldiguanide, the fluoro-analog of paludrine, has been synthesized by a modification of the method described by Curd and Rose[2] for the preparation of disubstituted diguanides. Pharmaceutical testing of the product is in progress.

Experimental[3]

***p*-Fluorophenyldicyandiamide.**—Exactly 33.0 g. (0.3 mole) of *p*-fluoroaniline[4] was added to 150 ml. of 5 *N* hydrochloric acid and diazotized by the addition of 21 g. (0.30 mole) of sodium nitrite in a saturated water solution while the temperature was maintained at 0–5°. The diazotized solution was added quickly with stirring to a solution of 28 g. (0.33 mole) of dicyandiamide[5] in 850 ml. of water at 20°. A total of 32 g. (0.25 mole) of sodium carbonate monohydrate was added in portions over the course of one and one-half hours, in order to maintain the alkalinity of the solution. The orange-red triazene which precipitated was separated by filtration and partially dried by means of a rubber dam.[6] It was then added in portions during the course of one hour to a stirred solution of 45 ml. of concentrated hydrochloric acid in 200 ml. of acetone at 10–15°. The mixture was stirred for two additional hours, 600 ml. of water was added, and the resulting green precipitate of crude *p*-fluorophenyldicyandiamide (28.0 g., 52%), m. p. 178–190°, was isolated by filtration. The product was purified by repeated treatment with charcoal in boiling 1 *N* sodium hydroxide solution, followed in each case by re-precipitation with hydrochloric acid, and finally by a single recrystallization from methanol. In this manner, 9.5 g. (18%) of almost colorless material melting at 204.0–205.4° was obtained.

Anal. Calcd. for $C_8H_7N_4F$: C, 53.9; H, 4.0; N, 31.5. Found: C, 54.0; H, 3.6; N, 31.3.

N^1-*p*-Fluorophenyl-N^5-isopropyldiguanide Monoacetate.—A mixture of 5.5 g. (0.03 mole) of *p*-fluorophenyldicyandiamide dissolved in 50 ml. of ethanol, 6 g. (0.10 mole) of isopropylamine and 3.9 g. of copper sulfate pentahydrate dissolved in 20 ml. of water was refluxed on a steam-bath for four days, during which time a red-brown precipitate was formed. The solvent and excess isopropylamine were then removed by distillation and a solution of 15 ml. of concentrated hydrochloric acid in 150 ml. of water was added. Hydrogen sulfide was bubbled into the mixture until no further precipitation occurred, the solid material was removed by filtration, and the filtrate was poured in a thin stream into a 20% solution of sodium hydroxide. The N^1-*p*-fluorophenyl-N^5-isopropyldiguanide separated as a gummy precipitate.

Inasmuch as the free base is difficult to recrystallize, the product was isolated as the acetate, as follows: the crude base was extracted from the mixture with ether, the ether extract dried over anhydrous sodium sulfate, and the ether removed. The residue was dissolved in dry toluene and the filtered solution treated with glacial acetic acid until a strong odor of acetic acid persisted. The precipitate was filtered, washed with toluene, and dried to yield 7.4 g. (82%) of colorless, non-hygroscopic, water-soluble crystals of N^1-*p*-fluorophenyl-N^5-isopropyldiguanide monoacetate, melting at 169–171°. Recrystallized from 2-butanone, the pure material melted at 171.2–172.1°.

Anal. Calcd. for $C_{13}H_{20}O_2N_5F$: C, 52.5; H, 6.8; N, 23.6. Found: C, 52.6; H, 6.6; N, 23.4.

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[1] The authors are indebted to the Office of Naval Research for a grant which made this and continuing investigations possible.

[2] Curd and Rose, *J. Chem. Soc.*, 729 (1946).

[3] All melting points are corrected; boiling points are uncorrected.

[4] Prepared by the method of Bradlow and VanderWerf, THIS JOURNAL, **70**, 654 (1948).

[5] Obtained through the courtesy of American Cyanamid Company.

[6] A sample of the triazene which had been dried and then purified by re-precipitation from sodium hydroxide solution decomposed at 124–126° with gas evolution.

3,4-Dichlorotetramethylene Sulfone

BY T. EARL JORDAN AND FRANK KIPNIS[1]

It has been found that following the method of Van Zuydewijn[2] which involved passing chlorine into a boiling solution of butadiene sulfone in benzene, 3,4-dichlorotetramethylene sulfone is obtained in approximately 50% yield. By using, instead, sulfuryl chloride in 25% excess with a little iodine, the yield is 67% and with 100% excess, the yield is 92–93%. Attempts to chlorinate further resulted in no definite compounds.

The preferred procedure is as follows: Butadiene sulfone is first prepared by the reaction of butadiene and sulfur dioxide in a bomb for several hours at about 100° and is recrystallized from alcohol. To a solution of 118 g. (1 mole) of this substance in 800 ml. of benzene containing a small crystal of iodine and maintained at 55–60° in a two-liter flask provided with a reflux condenser, stirrer and calcium chloride guard tube, 160 ml. (240 g.) of sulfuryl chloride is added with stirring during two and a half hours, after which stirring is continued for three hours at the same temperature. Excess sulfuryl chloride and the benzene are recovered by distillation at atmospheric pressure, after which the product distils at 145–150° under 5 mm. pressure; m. p. 99–100°. Recrystallization from *n*-butanol gives colorless crystals, m. p. 124°; yield 176 g. (93%). The product is soluble in acetone, cyclohexanone, hot

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[1] Present address: Oxford Products, Inc., Cleveland, Ohio.

[2] Van Zuydewijn and E. de Roy, *Rec. trav. chim.*, **57**, 445 (1938).