
NOTES

The Preparation of Ureas

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The nitrourea method for the preparation of ureas¹ is much superior to the old cyanate method. However, it can be further improved, particularly when the amine is sparingly soluble in water, or when steric effects interfere, by using 95% alcohol in place of water. Davis and Blanchard¹ used 50% alcohol in only one case and the impression gotten from their paper is that alcohol is liable to lead to complications. As a matter of fact, alcohol gives better yields, a purer product and a smoother reaction. In a number of cases examined the same product was obtained using either alcohol or water.

The method is simply to take 1 mol of amine, 1.15 mols of nitrourea and 4 to 5 vols. of 95% alcohol, and warm the mixture cautiously and slowly on a steam-bath, taking care that the evolution of gas does not become too rapid. When the reaction has slowed down, most of the alcohol is boiled off and the residual urea worked up from a suitable solvent.

As examples² (yield with water first, alcohol second), ethyl-*m*-toluidine gave 44 and 61% of the urea; *n*-propyl-*o*-toluidine, 14 and 74%; *n*-propyl-*m*-toluidine, 21 and 66%; *n*-propyl-*p*-toluidine, 68 and 85%; *n*-butylaniline,¹ 35 and 91%; and *n*-butyl-*o*-toluidine, 18 and 80%. The alcohol product was of the same (or higher) degree of purity as the water product. Ureas from other types of amines give similar results.

(1) Davis and Blanchard, *THIS JOURNAL*, **51**, 1790 (1929).

(2) Hjort, deBeer, Buck and Ide, *J. Pharmacol.*, **55**, 152 (1935).

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The Gel System: Cellulose Nitrate-Copper Bronze¹

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In a study of the phenomenon of gelation of solutions of cellulose nitrate by bronzing powders, some interesting relationships between the viscos-

(1) Some of the data reported here were also used in the preparation of a thesis for the degree of Chemical Engineer awarded to W. E. Gloor by the Case School of Applied Science, June, 1934.

ity of the cellulose nitrate and the amount of reagent causing solidification were found.

When very small amounts of both bronzing powders and copper salts are added to cellulose nitrate solutions, a clear solid gel of deep emerald green color results.² The following facts indicate that this gelation is caused by a reaction between copper in some form and the nitrate group in the cellulose ester. (a) When cuprous or cupric salts only are added to a solution of cellulose nitrate, neither gel nor color appears. (b) Deep colors and gels are obtained when bronzing powder and a copper salt are both added to a solution of a cellulose ester only when the ester is a nitrate. (c) Deep colors or gels are obtained only when either the metallic powder or soluble salt added contains copper, it being sufficient if either one of these ingredients contains copper.

From the fact that these gels are broken almost immediately when small amounts of water or 1% alcoholic fuchsin solution are added, and also lose their characteristic color, it is to be inferred that the combination between copper and the (presumably reduced) nitrate group is not one involving primary valences; rather would it seem to be due to a secondary valence or coordination linkage. The copper-nitrate complex seems less stable than the association compound between the system and the dye or water.

The data in Table I show the amount of gelling agent (a mixture of equal parts by weight of "gold" bronze (90% Cu, 10% Zn) and CuCl₂·2H₂O) needed to produce a strong gel, *i. e.*, one that will not flow on inverting the container, in 6% solutions of different viscosity cellulose nitrates of

TABLE I

Viscosity of N. C., ^a sec.	0.5	4	40	400
Sp. visc. of 0.1% soln. in anhy. EtOH	0.053	0.128	0.196	0.271
Rel. molecular weight	1	2.4	3.7	5.1
% gel agent to give gel	0.25	0.14	0.06	0.04
C ₆ units per mol of Cu	10.6	19.1	44.6	66.9
Relative no. C ₆ units per mol. Cu	1	1.8	4.2	6.4
Wt. N. C. per 63.56 g. of Cu	2710	4940	11420	17130

^a Standards A. S. T. M. D301-33, 1933, pp. 719-720, Formula A.

(2) U. S. Patent 2,001,170, May 10, 1935.

11.5% N_2 content dissolved in anhydrous ethyl alcohol containing 0.5% benzene. Relative molecular weights of the nitrocelluloses are calculated on the basis of Staudingers' equation $M = KcN_{sp}$, which becomes, for the following data, using 1/2-sec. cellulose nitrate as the unit: $M_x = N_{sp}/0.053$.

Also, the amount of gelling agent needed to produce a strong gel, and the concentration of cellulose nitrate in solution are related as shown in Table II.

TABLE II

Concn. "A. S." 40 sec. N. C. in anhyd. 2B EtOH, % by wt.	2	4	6	8
% gelling agent for gel	0.15	0.10	0.06	0.06
No. C_6 units per mol of Cu	5.1	15.1	44.6	59.5
Mols of Cu per C_6 unit	0.196	0.066	0.022	0.017

The correspondence, shown in Table I, between chain length of nitrocellulose and the number of C_6 units per molecule of Cu in the gel stage (assuming that the gel structure is about the same regardless of whether cellulose chains or Cu-nitrate links go to construct it) is a direct piece of evidence that the macromolecules of cellulose nitrate in solution are essentially linear or string-like.

This conception leads to a simple picture of nitrocellulose gel formation, namely, that the chain molecules are joined at points along their length by the Cu-nitrate complex formation, giving a gel structure. The greater the length of these chains, or the greater their concentration, the less gelling agent is required to give a solid gel. These data also give an approximate portrayal of a simple three-dimensional gel structure, the cellulose chains being the linear bonds cross-linked by the copper-nitrate complex.

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The Optical Rotation of *l*-Threose

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The recent work of Robert C. Hockett¹ has shown values for the specific rotations of *d*-threose diacetamide ($[\alpha]_D -10.9^\circ$ in water) and *d*-threose ($[\alpha]_D -12.3^\circ$ in water) which are in full disagreement with values which we have published² for *l*-threose diacetamide ($[\alpha]_D -7.7^\circ$ in water) and *l*-threose ($[\alpha]_D -24.6^\circ$ in water).

(1) Hockett, *This Journal*, **57**, 2260, 2265 (1935).

(2) Deulofeu, *J. Chem. Soc.*, 2458 (1929).

One must of course expect from stereochemical theory that enantiomorphous isomers will have rotations of equal magnitude but opposite signs. Undoubtedly Hockett is right in his rotations. Some time ago we measured the rotation of *d*-threose diacetamide and found $[\alpha]_D -10.4^\circ$ in water (0.2205 g. in 5 cc. rotated -0.93° in a 2-dm. tube). A sample with an initial rotation of -9.9° in 0.3 *N* sulfuric acid (0.2238 g. in 5 cc. rotated -0.89° in a 2-dm. tube) was hydrolyzed by heating for forty-five minutes in a boiling water-bath, and the rotation changed to -15.1° . (The reading was -0.74° .) The assumption was made in calculating this last reading that all the diacetamide compound has been hydrolyzed and transformed into *d*-threose, an assumption that Hockett shows to be erroneous. That explains why, although the reading was a little inferior to the initial, the calculation gave a higher value for the rotation.

In this connection, following the same method employed for the preparation of triacetyl *l*-erythreose diacetamide,³ we prepared triacetyl *d*-threose diacetamide melting at $176-177^\circ$ (uncorr.) and found $[\alpha]_D +38^\circ$ in water (0.1124 g. in 5 cc. rotated $+1.71^\circ$ in a 2-dm. tube). It is evident that the compounds of the *l*-series must be corrected for its sign and values. The only explanation for our inversion of the sign is that an error was done when noting it. We have no explanation for the sign of rotation given by Freudenberg, which we interpreted when published as confirming our own.

(3) Deulofeu, *J. Chem. Soc.*, 2973 (1932).

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A Measure of Acidity Obtained from the Electromotive Force of a Cell without Liquid Junction

By DAVID I. HITCHCOCK

The value of hydrogen-ion determinations in many branches of chemistry has been established beyond question. The usual units of acidity, *pH* and *paH*, as defined by Sørensen,¹ are theoretically unsatisfactory because they are based on the assumption that the concentration or activity of the hydrogen ion can be obtained by the use of a cell

(1) Sørensen, *Compt.-rend. trav. lab. Carlsberg*, **8**, 1 (1909); Sørensen and Linderstrøm-Lang, *ibid.*, **15**, No. 6 (1924).