NOTES

The Preparation of Ureas

By Johannes S. Buck and Clayton W. Ferry

The nitrourea method for the preparation of ureas[1] 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 Blanchard[1] 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 examples[2] (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 Bronze[1]

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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 viscosity 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 coördination 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 $CuCl_2 \cdot 2H_2O$) 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.

(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.

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