

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE VIRGINIA POLYTECHNIC INSTITUTE]

THE ACTION OF SODIUM ON CELLULOSE IN LIQUID AMMONIA

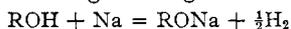
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The action of sodium hydroxide solutions upon cellulose to form a compound of cellulose which has attained commercial importance in the viscose process has long been known.¹ The constitution of the compound formed in this reaction has never been definitely established although, reasoning from analogy with the ordinary alcohols, it has been assumed to be of a sodium alcoholate type in which the hydrogen atom of one, or possibly more, hydroxyl groups is replaced by sodium. Definite proof of such a compound is, however, lacking and the authors in this research have attempted to supply some evidence of it.

Kraus and his students² have shown that when an alcohol is treated with sodium in liquid ammonia, a sodium alcoholate results and an atom of hydrogen is liberated according to the general reaction



In applying this general reaction to cellulose several points were investigated. First, the amount of hydrogen obtainable from a definite amount of sodium reacting with cellulose was carefully determined and was found to agree very closely with the above reaction. Second, the final product was examined and found to possess in full the property of normally prepared soda cellulose, of reacting with carbon bisulfide to form xanthates completely soluble in water or alkali. This reaction is treated in more detail in another paper.³ Third, it was found that there was no appreciable amount of sodium amide formed as a product of the reaction of the sodium with the solvent. The hydrogen evolved in the experiments, then, could only have come from the reaction of the sodium upon the cellulose. Fourth, it was found that one atom of hydrogen per $\text{C}_6\text{H}_{10}\text{O}_5$ group was rapidly and easily displaced. The succeeding atoms of sodium entered very slowly, due possibly to the formation of a film of rather insoluble soda cellulose about the fibers. This slower rate of reaction might also be due to lesser affinity of the secondary alcohol groups for the sodium or to an overloading of the molecule with such a strongly positive atom as sodium. No matter in what excess nor for how long a time such an excess of sodium was allowed to react upon cellulose, no more than three atoms of sodium per $\text{C}_6\text{H}_{10}\text{O}_5$ group could be introduced into the molecule. This reaffirms

¹ Cross and Bevan, *Chem. News*, **63**, 66 (1891).

² Kraus and White, *THIS JOURNAL*, **45**, 768 (1923).

³ Hussey and Scherer, "Rate of Reaction between Carbon Disulfide and Soda Cellulose."

previous evidence from acetylation and nitration of the presence of only three hydroxyl groups per $C_6H_{10}O_5$ group.

A consideration of the above described results leads to the conclusion that cellulose reacts in liquid ammonia as a typical tribasic alcohol and that, by analogy, the product of its reaction with solutions of caustic soda is probably sodium cellulose alcoholate. The number of hydroxyl groups so converted by sodium hydroxide solution probably depends upon the conditions of the reaction. Soda cellulose prepared by the action of metallic sodium in liquid ammonia is being used in this Laboratory as a material for an investigation of its reactions with other reagents.

Experimental Part

Apparatus.—As indicated in the sketch, the reaction tube consisted of a Pyrex glass test-tube (A), 32 by 300 mm., immersed in a Dewar tube (B) containing liquid ammonia boiling at atmospheric pressure.

Tube (C) which passed through the rubber stopper of the reaction tube was a T tube in which the sodium to be added could be suspended by means of the movable rod (D). This tube also served to connect the reaction vessel to either the manometer (F) or the eudiometer (G) through the two-way stopcock (E). The manometer served as the apparatus and to supply the pressure necessary to condense ammonia in (A). The hydrogen evolved was collected over water in order to remove the gaseous ammonia.

The ammonia was dried by passing over fused potassium hydroxide in the two towers (K) and then through a tube (J) packed with carefully dried Bentonite and the train was kept free of moisture and air by the mercury seals (I).

Procedure and Materials.—In order to prove the absence of water in the condensed and gaseous ammonia, about 50 cc. of ammonia from the train was condensed in (A) and 0.1 g. of freshly cut sodium was suspended in tube (D). After all gases had been blown out by a rapid current of ammonia, the sodium was dropped into the condensed ammonia. Absolutely no hydrogen was collected even after several hours.

The sodium used in the experiments was freshly cut under low boiling petroleum ether, weighed in Nujol, washed carefully in petroleum ether and then introduced into tube (D).

The cellulose used in these experiments was of three types. The first was a standard cellulose prepared from absorbent cotton according to the method described by Corey and Gray.⁴ This contained 98.7% alpha cellulose and 0.10% ash.

The wood pulp cellulose was prepared by finely dividing and carefully drying Brown Company alpha pulp containing 94.67% alpha cellulose and 0.136% ash.

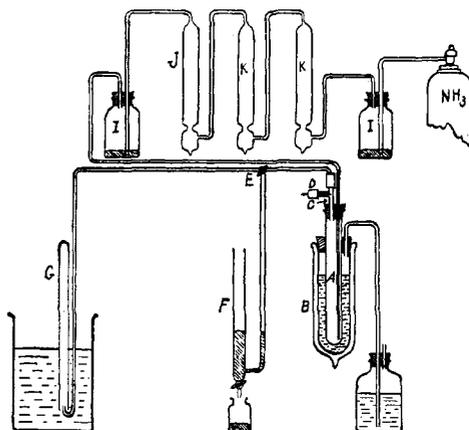


Fig. 1.

⁴ Corey and Gray, *Ind. Eng. Chem.*, 16, 853 (1924).

The regenerated cellulose used was prepared by finely dividing and carefully drying bleached and desulfurized viscose rayon prepared from Brown Company alpha pulp.

In all the experiments a sample of cellulose, accurately weighed in a weighing bottle, was placed in the reaction tube and about 50 cc. of ammonia condensed on it under a pressure of about 15 cm. of mercury in the manometer. The pressure was released by running mercury from the manometer and, with a rapid stream of ammonia passing, the tube (D) was opened and the weighed sodium suspended therein. The tube was closed and the apparatus was freed of traces of air and petroleum ether by a current of ammonia. By means of the two-way stopcock the apparatus was connected to the eudiometer and the sodium was dropped into the reaction vessel. A vigorous reaction ensued which was timed from the first addition of the sodium to the disappearance of all trace of the characteristic blue color of free sodium. After careful sweeping, the collected gas was measured and analyzed.

The residue in the reaction tube was allowed to settle and was washed several times by condensation of fresh portions of ammonia upon it. The liquid was removed each time by suction and evaporated under reduced pressure. After warming to drive out ammonia, the infinitesimal residue was dissolved in water and was of sufficient alkalinity to turn phenolphthalein. One drop of *N*/10 sulfuric acid was sufficient to turn the solution acid and it was concluded that no sodium amide resulted from the reaction. The cellulosic residue, as described in another paper,³ gave typical xanthates.

Results

The results were compiled into tables for ease of comparison and are given herewith.

EXPERIMENTS WITH STANDARD CELLULOSE

Ratio cellulose/sodium	Cell, g.	Sodium, g.	Time, min.	Atoms of H ₂ per atom of sodium
1:0.228	1.8432	0.0596	4	0.983
1:0.504	0.4215	.0299	3	1.049
1:0.750	.6868	.0731	13	1.022
1:1.000	.3556	.0505	...	1.020
1:0.984	.4408	.0616	7	1.019
1:1.24	.4208	.0741	28	1.002
1:1.25	.3520	.0625	35	0.991
1:1.50	.3045	.0650	90	.974
1:2.03	.2381	.0682	240	.919
1:2.99	.1420	.0603	200	.960
1: excess	.2476	.1977	420	2.979 ^a

EXPERIMENTS WITH WOOD PULP CELLULOSE

1:0.250	1.6243	0.0577	2	0.983
1:0.494	0.7712	.0544997
1:0.760	.7414	.0800	4	.962
1:0.949	.7054	.0950	5	1.003
1:0.990	.5284	.0743	9	0.990
1:1.23	.3533	.0617958
1:1.47	.2471	.0515	...	1.044
1:1.68	.3393	.0809	...	0.993
1:1.99	.1948	.0551	120	.934
1:3.00	.1608	.0686	137	.963
1: excess	.1518	.1288	337	3.050 ^a

EXPERIMENTS WITH REGENERATED CELLULOSE

Ratio cellulose/sodium	Cell, g.	Sodium, g.	Time, min.	Atoms of H ₂ per atom of sodium
1:0.250	1.8262	0.0648	...	1.000
1:0.496	0.8726	.0615	2	1.003
1:0.832	.4995	.0531	...	1.035
1:1.01	.4496	.0644	5	1.005
1:1.50	.2761	.0587	24	1.013
1:1.97	.1815	.0508	30	1.014
1:2.47	.1976	.0692	113	0.961
1:2.93	.1358	.0564	150	.925
1: excess	.2532	.2310	240	2.949 ^a
General average				0.990

^a These values give the atoms of hydrogen replaced per C₆H₁₀O₅ group, the general average of which is 2.993 atoms.

Summary

1. The action of metallic sodium on cellulose in liquid ammonia has been studied.
2. One atom of sodium enters the molecule rapidly, whereas the second and third enter very slowly.
3. A maximum of three atoms of sodium per C₆H₁₀O₅ group enters the molecule.
4. The reaction corresponds in general to the ordinary alcoholate reaction, ROH + Na = RONa + $\frac{1}{2}$ H₂.
5. It is concluded that cellulose acts as an alcohol in liquid ammonia and probably does so in its other reactions in other solvents.

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[JOINT CONTRIBUTION FROM THE FOOD RESEARCH DIVISION, BUREAU OF CHEMISTRY AND SOILS, AND MICROANALYTICAL LABORATORY, FOOD AND DRUG ADMINISTRATION, UNITED STATES DEPARTMENT OF AGRICULTURE]

THE IDENTIFICATION OF MESAONIC ACID¹

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During an investigation of the occurrence of organic acids in plant material, interest was aroused in the true melting point of mesaconic acid, and also in the preparation and physical and chemical properties of some new derivatives which might prove useful in its identification. Of the derivatives commonly used, the amide is the only one which previously has been reported, but since the hydrazide is the most easily prepared, when the ester is available, it has been the derivative most commonly used in this Laboratory for the identification of naturally occurring organic acids.

¹ Food Research Division Contribution No. 103.