of oxidant (straight-chain or cyclic) of a particular system.

Summary

The oxidation–reduction potentials of systems whose reductants are substituted thioureas have been measured in acid solutions and the E_0' determined.

Compounds whose reductants contain two thiourea type (thioureido-) groups have also been measured. Their oxidants are cyclic disulfides: the largest ring oxidant studied contained eight atoms and the two S atoms.

ST. LOUIS, MISSOURI RECEIVED DECEMBER 18, 1948

[CONTRIBUTION FROM THE WOOD CHEMISTRY LABORATORY OF THE DIVISION OF FORESTRY, UNIVERSITY OF MINNESOTA]

Hydrogen Bonding and the Swelling of Wood in Various Organic Liquids[1,2]

BY AMAR NATH NAYER AND RALPH L. HOSSFELD

Many attempts have been made to account for the swelling of wood, cellulose, and other colloidal substances when in contact with swelling agents. By and large, the net result has been the development of general theories based on the Donnan equilibrium,[3] adsorption of ions and their associated sphere of water of hydration,[4] and selective adsorption of ions with a resulting repulsion of colloidal surfaces of like charge.[5] Other workers have attempted more specifically to relate the phenomenon of swelling to the dielectric constant[6] and to the zeta potential[7] of the swelling liquid with respect to wood and cellulose. According to Stamm, however, none of these theories will adequately explain the swelling of wood in all the many types of swelling agents which have been studied.[8]

Recently Gordy[9,10] made use of the infrared absorption in studying the phenomenon of hydrogen bonding. He measured the wave length of the characteristic absorption band corresponding to the OD vibration in MeOD dissolved in benzene. In certain solvents, other than benzene, he observed a shift ($\Delta\mu$) in this wave length and attributed this shift to the formation of hydrogen bonds (actually deuterium bonds) between methyl alcohol and the solvent. The fact that Gordy found a very large value for $\Delta\mu$ in pyridine and the fact that pyridine is known to swell wood very appreciably, suggested that hydrogen bonding between hydroxyl groups in wood and added liquids may account for the swelling of wood in these liquids.

The relationship between the $\Delta\mu$ for the compounds as determined by Gordy and the degree of swelling of maple wood in these same compounds is shown in Fig. 1. It is apparent that a majority of the data indicates a direct relationship between the degree of swelling and the hydrogen bonding as determined by Gordy. Most notable exceptions to the relationship are the data for di-*n*-butylamine, tri-*n*-butylamine, N-methylaniline, N-dimethylaniline, quinoline and quinaldine.

In explanation of these exceptions, there is much evidence that molecular size might be an important factor.[7,11,12,13,14] However, determination of the swelling of maple wood by several homologous series of amines indicated that molecular structure as well as size might be important. In the series of methyl pyridines, the position of the methyl group was found to affect the swelling although the molecular size of the swelling agents was not greatly different.

The work of Brown and Barbaras[15] has shown, however, that the steric hindrance offered by a methyl group in the 2-position of pyridine decreased the stability of the resulting association compound with trimethyl boron. They have also shown that the steric effect in association compounds of trimethyl boron with secondary and tertiary aliphatic amines is in the order of increasing substitution on the nitrogen atom. Steric hindrance appears, therefore, to be a large factor in the strength of association between donor and acceptor atoms.

The majority of the OH groups in the cellulose molecule of wood may be in effect those of a substituted methyl alcohol R-(CHOH)-R′ where R and R′ represent portions of the cellulose molecule and as such would be subject to steric hindrance. It would, therefore, be predicted from Gordy's work that piperidine should be capable of swelling wood to a greater extent than pyridine and that 2-picoline should fall between these two.

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(1) From a thesis by A. N. Nayer presented to the Graduate Faculty of the University of Minnesota in partial fulfillment of the requirements for the Ph.D. degree, March, 1948.

(2) Paper No. 2457 in the Scientific Journal Series of the Minnesota Agricultural Experiment Station, St. Paul, Minnesota.

(3) Proctor and Wilson, *J. Chem. Soc.*, **109**, 307 (1916).

(4) Pauli and Handkowsky, *Biochem. Z.*, **18**, 340 (1909).

(5) Tarkow, Stamm and Erickson, Mimeo Report No. 1593, U. S. Forest Prod. Lab., Madison, Wis., 1946.

(6) De Bruyn, *Nature*, **142**, 570 (1938).

(7) Stamm, *Ind. Eng. Chem.*, **27**, 401 (1935).

(8) Stamm, "Wood Chemistry," A. C. S. Monograph No. 97, edited by Wise, Reinhold, New York, 1944, Chapter 13.

(9) Gordy, *J. Chem. Phys.*, **7**, 93 (1939).

(10) Gordy and Stanford, *ibid.*, **9**, 204 (1941).

(11) Davis, Barry, Peterson and King, THIS JOURNAL, **65**, 1294 (1943).

(12) Erickson and Rees, *J. Agr. Research*, **60**, 593 (1940).

(13) Kress and Bialkowski, *Paper Trade J.*, **93**, No. 20, 35 (1931).

(14) Sheppard and Newsome, *J. Phys. Chem.*, **36**, 2306 (1932).

(15) Brown and Barbaras, THIS JOURNAL, **69**, 1137 (1947).

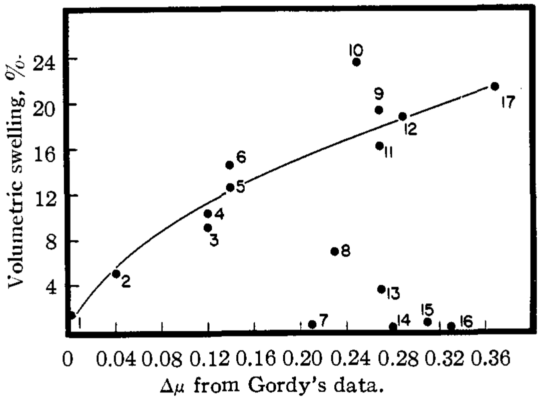

Fig. 1.—Intensity of hydrogen bonding and the swelling of maple wood: 1, benzene; 2, nitrobenzene; 3, ethyl acetate; 4, benzaldehyde; 5, acetone; 6, dioxane; 7, N-dimethylaniline; 8, N-methylaniline; 9, pyridine; 10, *n*-butylamine; 11, aniline; 12, 2-picoline; 13, quinoline; 14, quinaldine; 15, di-*n*-butylamine; 16, tri-*n*-butylamine; 17, piperidine.

By reason of the inductive effect of the two methyl groups on the nitrogen in 2,6-lutidine, we might predict that this compound would swell wood to a greater extent than 2-picoline. Because of the steric effect pointed out by Brown, however, we are led to modify these predictions such that the order of swelling of wood in these compounds would be: piperidine > pyridine > 4-picoline ≅ 3-picoline > 2-picoline > 2,6-lutidine. These predictions are borne out in the curves of Fig. 2.

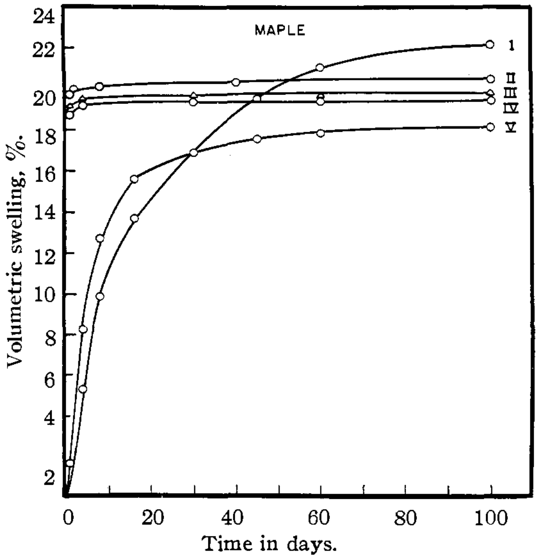

Fig. 2.—Swelling of maple in piperidine and homologous pyridines: I, piperidine; II, pyridine; III, 3-picoline; IV, 2-picoline; V, 2,6-lutidine.

In considering the homologous series of anilines, it would be predicted that the degree of swelling effected by the various members would be in the order: aniline > N-methylaniline > N-ethylaniline > N-dimethylaniline > N-diethylaniline. This again is substantiated in the curves of Fig. 3.

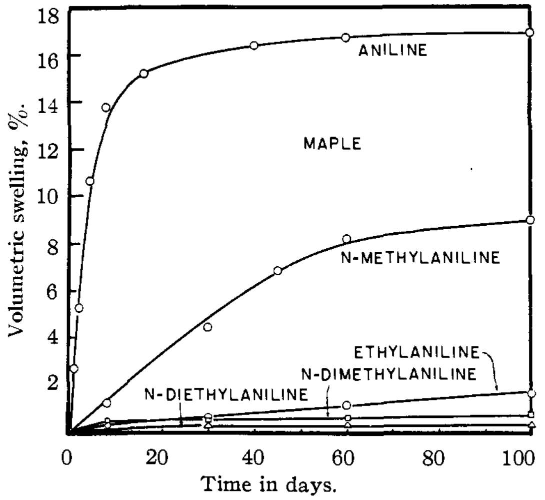

Fig. 3.—Swelling of maple in various anilines.

Figure 4 illustrates the observation that the group of primary aliphatic amines approaches a common swelling value. This is in agreement with Gordy's observation[16] that the $\Delta\mu$ of D_2O varied only slightly in the series of aliphatic amines which he studied.

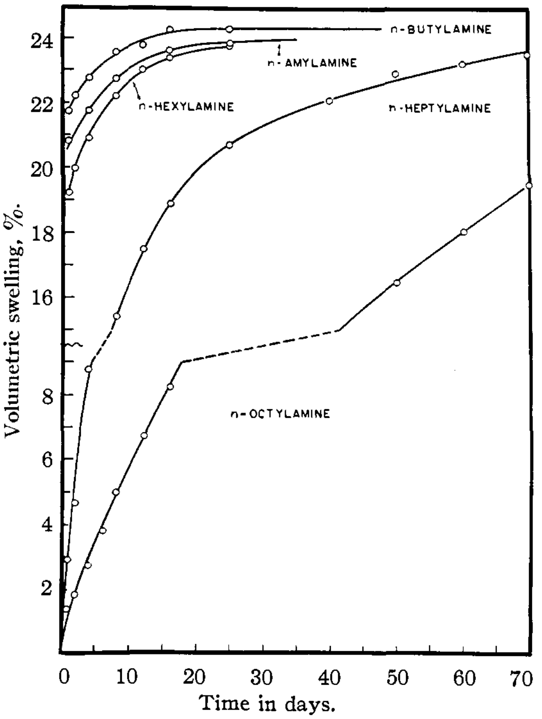

Fig. 4.—Swelling of maple in primary aliphatic amines.

Turning again to Fig. 1, the wide divergence of the points noted above appears to be explained on the basis of steric hindrance. It is felt that

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(16) Gordy, *J. Chem. Phys.*, 9, 215 (1941).

sufficient agreement exists among the data to permit the proposal that the degree of swelling bears a direct relationship to the intensity of hydrogen bonding between the constituents of wood and the swelling agent and that steric hindrance is a controlling influence on the intensity of the hydrogen bonding.

It must be pointed out, however, that the generality of this working hypothesis is subject to reservations for the present in its application to woods other than maple. A similar study of the swelling of Sitka spruce has shown general agreement with the results of the present study. However, certain points of disagreement have appeared which may be related to differences in chemical composition between the two species of wood. This observation is being made the subject of further study.

TABLE I

VOLUMETRIC SWELLING OF SUGAR MAPLE[a]

Swelling agent	$\Delta\mu$ from Gordy[9,10]	Swelling after 90 days, %
Water	..	16.12
Acetone	0.14	12.60
Ethyl acetate	.12	9.14
Dioxane	.14	14.43
Morpholine	..	20.87
Ethyl cellosolve	..	15.60
Benzene	0	1.42
Benzaldehyde	.12	10.32
Nitrobenzene	.04	5.19
Piperidine	37	21.16
Pyridine	.27	19.38
2-Picoline	.29	18.79
3-Picoline	..	19.08
4-Picoline	..	19.17
2,6-Lutidine	.	17.38
Isoquinoline	..	3.24
Quinoline	.27	3.54
Quinaldine	.28	0.23
Aniline	.27	16.16
N-Methylaniline	.23	6.90
N-Dimethylaniline	.21	0.42
N-Ethylaniline	..	1.60
N-Diethylaniline	..	0.21
Diethylamine	..	17.66
Triethylamine	..	0.83
n-Butylamine	.25	23.47
Di-*n*-butylamine	.31	0.71
Tri-*n*-butylamine	.33	0.34

[a] Expressed as per cent. of original oven-dry dimension. Values are average of four replicate specimens.

Experimental

Most of the compounds used as swelling agents in this study were obtained from Eastman Kodak Company and were of white label quality. The normal amyl, hexyl, heptyl and octylamines were generously supplied by Sharples Chemicals, Inc. All of the compounds were carefully purified by drying over suitable drying agents and distilling through an efficient fractionating column. The amines were allowed to stand in contact with solid potassium hydroxide; and the dioxane, benzene, and morpholine were refluxed with metallic sodium before fractionation. The acetone, ethyl acetate, and ethyl cellosolve were dried over anhydrous sodium sulfate before fractionation. Benzaldehyde was extracted with aqueous sodium bicarbonate, dried over anhydrous calcium chloride, and fractionally distilled.

Preparation of Wood Sections.—All samples were taken from an unseasoned 2 in. × 10 in. × 16 ft. flat sawn board of sugar maple (*Acer saccharum* Marsh) containing mostly sapwood. The moisture content at the time of acquisition was 20–25%. The specific gravity based on the oven dry weight and green volume varied from 0.58 to 0.61. Pieces measuring 2 × 2 × 48 inches were cut from the board and seasoned to a moisture content of 8–9% in a controlled humidity chamber, and in the air dry condition they gave an average of 16 annual rings per inch. These pieces were selected so that the position of the annual rings was parallel to one dimension of the cross section. The finally selected pieces were planed and sawed into thin cross-sections, dimensions of which were 40 mm. in the tangential direction, 32 mm. in the radial direction, and 4 mm. in the longitudinal direction, with the annual rings parallel to the longest dimension. In a typical experiment, the required number of sections were numbered and dried in a vacuum oven for twenty-four hours at a temperature of 65 ± 2° and under a vacuum of at least 27 in. of mercury. On removal from the oven, the sections were cooled in a desiccator, quickly measured with a micrometer caliper to the nearest 0.005 mm. in the radial and tangential dimension, and placed in sealed one-pint Mason jars containing the swelling agent. At the designated intervals, the jars were opened, the dimensions of the specimens again measured, and the specimens immediately returned to the jar and sealed. All experiments were carried out at room temperature (25–30°).

Since it was found that small amounts of water in the organic swelling media had a great effect in many cases on their ability to swell wood, precaution was taken to ensure that the swelling agents remained anhydrous. As a control measure, a series of experiments was made in which sections were allowed to remain sealed in jars of the swelling liquid for a period of ninety days after which they were measured and compared with the previous experiments where the sections were exposed periodically to the moisture of the air in the course of taking measurements. The agreement was believed to be satisfactory.

The per cent. of swelling of the wood sections was calculated according to the formula

$$\text{Per cent. swelling} = \frac{(\text{Swollen dimension} - \text{Oven-dry dimension})}{(\text{Oven-dry dimension})} \times 100$$

Since the swelling in the fiber direction was negligible in normal wood, the sum of the values for the tangential and radial swelling was taken to be equal to the per cent. volumetric swelling of the wood section.[17]

Acknowledgment.—The authors wish to acknowledge coöperation of Dr. A. J. Stamm and Dr. Harold Tarkow of the Forest Products Laboratory, Madison, Wisconsin, under whose direction this work was initiated during a period of study by one of us (A. N. Nayer) at that laboratory.

Summary

A study has been made of the swelling of maple wood (*Acer saccharum* Marsh) in a variety of organic liquids including several homologous series of amines. A correlation has been suggested between the degree of swelling and the

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(17) It is recognized that an error is involved in such an evaluation of the per cent volumetric swelling. However, sample calculations of the mathematically correct values showed that the error lacks significance.

extent of hydrogen bonding between the constituents of wood and the swelling agent. The observed swelling behavior of the wood is explained in the hypothesis, that the degree of swelling bears a direct relationship to the intensity of hydrogen bonding between the constituents of wood and the swelling agent and that steric hindrance is a controlling influence on the intensity of the hydrogen bonding.

ST. PAUL, MINNESOTA RECEIVED MARCH 5, 1949

[FROM THE CHEMISTRY LABORATORY OF THE STATE UNIVERSITY OF IOWA]

Removal of Chlorine from Aromatic Nitrochloro Compounds. Preparation of 1,3-Dinitronaphthalene

BY WALTER T. SMITH, JR.

1,3-Dinitronaphthalene has been prepared by various procedures,[1] all of which involve 1-amino-2,4-dinitronaphthalene as an intermediate and the subsequent removal of the amino group by diazotization and reduction. A new method for preparing 1,3-dinitronaphthalene has been discovered which depends on dehalogenation of 1-chloro-2,4-dinitronaphthalene. This intermediate can be prepared easily and in good yield from α-naphthol.[2] The dehalogenation of 1-chloro-2,4-dinitronaphthalene is accomplished by heating it with copper powder in molten benzoic acid at 150–200°. The hydrogen which replaces the chlorine apparently comes from the carboxyl group of the benzoic acid. From this reaction mixture 1,3-dinitronaphthalene can be isolated in 74% yield.

Other acids of suitable boiling point can be substituted for benzoic acid. When the reaction is carried out in *n*-caproic acid (b. p. 205°) the yield of 1,3-dinitronaphthalene is somewhat lower (73% crude).

This use of an organic acid and copper as a means of removing chlorine from aromatic nitrochloro compounds explains Ullmann's isolation of 3,5-dinitrobenzoic acid in unspecified yield when 2-chloro-3,5-dinitrobenzoic acid was heated with copper in phenol.[3] During the present work a 77% yield of the copper salt of 3,5-dinitrobenzoic acid was obtained when 4-chloro-3,5-dinitrobenzoic acid was heated with copper in nitrobenzene. That the carboxyl group need not be in the same molecule as the chlorine is shown by our preparation of 1,3-dinitronaphthalene and by other reactions cited below. Rindl[4] also observed the formation of an appreciable amount of 1,3-dinitronaphthalene as a by-product in the preparation of 2,4,2′,4′-tetranitro-α,α′-binaphthyl. In this case the source of the hydrogen which replaces the chlorine is not known. It is suggested that the hydrogen may have come from traces of water in the nitrobenzene in which the reaction was carried out. This would be in keeping with reports in the literature that when picryl chloride and copper are heated in toluene hexanitrobiphenyl is obtained[5] whereas when the same reagents are heated in alcohol[6] trinitrobenzene is formed. In the present work 1,3,5-trinitrobenzene was obtained in only 20% yield by the action of copper on picryl chloride in boiling nitrobenzene containing an equivalent of benzoic acid.

In order to learn more about the generality of the reaction, the removal of chlorine from chloronitrobenzenes was also studied. 2,4-Dinitrochlorobenzene gave a 52% yield of 1,3-dinitrobenzene. *o*-Chloronitrobenzene gave a 59% yield of nitrobenzene. The *meta*-isomer gave at best only a small amount of nitrobenzene. With the *para*-isomer there was no evidence of the formation of nitrobenzene. The inactivity of the chlorine *para* to the nitro group is in keeping with the results of Ullmann[5] who found that although *o*-chloronitrobenzene gave a 60% yield of *o,o′*-dinitrobiphenyl, *p*-chloronitrobenzene gave unsatisfactory yields of the corresponding biphenyl and it was necessary to use the iodo compound in order to obtain comparable yields.

Experimental

1,3-Dinitronaphthalene.—To a hand-stirred mixture of 7 g. (0.057 mole) of benzoic acid and 5 g. (0.02 mole) of 1-chloro-2,4-dinitronaphthalene in a 50-ml. beaker was added 5 g. of copper powder (Baker and Adamson, fine powder) in several portions over a period of five minutes (temp. at 150–200°). After the melt solidified, the beaker was placed in 100 ml. of 10% sodium bicarbonate solution and the melt was digested until it was completely broken up and no effervescence was evident. The liquid suspension was filtered through a Soxhlet thimble. The material in the thimble was then extracted in a Soxhlet extractor with 100 ml. of acetone until no more color was extracted. Upon cooling and filtering the extract there was obtained 1.6 g. of 1,3-dinitronaphthalene, m. p. 145–146° (cor.). From the filtrate there was obtained 2.1 g. of material which after recrystallization from 35 ml. of aqueous pyridine weighed 1.9 g., m. p. 145–146° (cor.); total yield 3.2 g. (74%).

In another run *n*-caproic acid was substituted for benzoic acid. The product was isolated after removing

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(1) See for example, Hodgson, Birtwell and Marsden, *J. Chem. Soc.*, 112 (1944).

(2) Morgan and Evens, *J. Chem. Soc.*, **115**, 1128 (1919); Ullmann and Bruck, *Ber.*, **41**, 932 (1908).

(3) Ullmann and Engi, *Ann.*, **366**, 88 (1909).

(4) Rindl, *J. Chem. Soc.*, **103**, 1917 (1913).

(5) Ullmann and Bielecki, *Ber.*, **34**, 2177 (1901).

(6) Meyer, German Patent 234,726 (*Chem. Zentr.*, **82**, I, 1767 (1911)).