

dihydrogen phosphate. The rye amylase showed a range of optimum activity between PH 3.5 and 5.0 in the starch substrate as described.

Discussion of Results

It seems logical to consider that starch-digesting enzyme as obtained from various starch-storing grains might be the same substance. To throw light upon this hypothesis, enzyme material has been prepared from germinated wheat and rye by a method corresponding to that used for the preparation of purified enzyme from malt, and some of the properties of these amylase precipitates have been tested. The amylases from wheat and rye show the typical protein tests, as was indicated by the work of Sherman and Schlesinger for malt enzyme. The hydrogen-ion concentrations at which malt amylase exerts optimum activity has been determined by Sherman, Thomas and Baldwin⁹ at PH 4.4 to 4.6; the results obtained for optimum activity of wheat amylase at PH 4.5 to 5.1 and of rye amylase at PH 3.5 to 5.0 indicate a similarity in the activity of the amylases of these three cereal grains.

Summary

The amylases from germinated wheat and rye compare very favorably with amylase from malt described by Osborne and by Sherman and co-workers on the following points: (1) they are obtained by the same process of dialysis and fractional precipitation with alcohol; (2) they give the typical protein tests; and (3) they show optimum activity at a corresponding range of hydrogen-ion concentration in the starch substrate.

AMES, IOWA

[CONTRIBUTION FROM THE DEPARTMENT OF PHARMACOLOGY OF JOHNS HOPKINS UNIVERSITY]

THE INFRA-RED ABSORPTION SPECTRA OF ORGANIC DERIVATIVES OF AMMONIA. II. ALPHA-NAPHTHYLAMINE AND SOME MONO- AND DIALKYL-ALPHA-NAPHTHYLAMINES

BY FREDERICK K. BELL

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Introduction

In this, the second of a series of studies of the infra-red absorption of primary, secondary and tertiary amines, α -naphthylamine and some mono- and dialkyl- α -naphthylamines have been selected for investigation. Like the alkyl anilines, they represent mixed amines in which one aryl group is always present and one or two alkyl groups, corresponding to the secondary or tertiary amine, respectively, are introduced.

Coblentz¹ measurements of naphthalene, dissolved in carbon tetra-

⁹ Sherman, Thomas and Baldwin, *THIS JOURNAL*, **41**, 231 (1919).

¹ Coblentz, *Carnegie Inst. Publ.*, No. **35**, 127 (1905).

chloride, for a restricted region in the shorter infra-red, Stang's² investigations between 1.0 and 10.0 μ of the absorption of both carbon tetrachloride and carbon disulfide solutions of naphthalene, α - and β -naphthylamine, α - and β -naphthol and α -nitronaphthalene, and the author's results³ in the case of molten naphthalene at 95°, are apparently the only references in the literature concerning the infra-red absorption of compounds containing the naphthyl group.

In the present study, the absorption spectra of molten α -naphthylamine at 60°, mono- and dimethyl- α -naphthylamine, and mono- and diethyl- α -naphthylamine have been examined as far as 12.0 μ and it will be of particular interest to observe whether the spectra of these compounds display the same qualitative differentiation between the primary and the secondary and the tertiary amino groups as was found in the case of aniline and the alkyl anilines.

Experimental Part

All of the substances investigated in the present study were obtained from the Eastman Kodak Company and were designated as of "highest purity."

The complete description of the experimental method employed in the determination of infra-red absorption spectra has been fully treated in a previous paper.⁴

All of the alkyl- α -naphthylamines selected for study are liquids at ordinary temperature. α -Naphthylamine, which melts at 50°, was retained in the molten state during investigation by means of an electrical heating device previously described.⁵ Similarly, β -naphthylamine m. p. 110°, was examined in the molten state at 125° by means of this same device. The absorption curve obtained for this compound has been omitted in the present paper.

The absorption spectra are shown graphically in Figs. 1, 2 and 3. In these curves the percentage transmission has been plotted against the wave length in microns. The values of T , indicating the thickness of the absorbing layer used, are noted in each curve.

Discussion

The absorption curve for α -naphthylamine as shown in Fig. 1 confirms, in its general features, the results obtained by Stang⁶ for carbon tetrachloride and carbon disulfide solutions of this substance. The broad band obtained by him at 3.1 μ has been resolved into two bands, at 2.9 μ and 3.2 μ . Likewise at 5.2 μ two bands appear, at 5.1 μ and at 5.4 μ in the present curve. Bands at 6.1 μ , 6.8 μ , 7.1 μ , 7.7 μ , 8.5 μ , 8.9 μ , 9.1 μ ,

² Stang, *Phys. Rev.*, **9**, 542 (1917).

³ Bell, *THIS JOURNAL*, **47**, 2811 (1925).

⁴ Ref. 3, p. 2194.

⁵ Ref. 3, p. 2812.

⁶ Ref. 2, p. 550.

and 9.8μ appear in both curves. If the present curve be regarded as a standard of comparison, it is interesting to note the influence of the solvent on the absorption as shown in Stang's curves.

When compared with the absorption of naphthalene, that of α -naphthylamine shows a great reduction in the general transparency to infra-red radiation. This strongly suggests the similar relation that has been found to exist between benzene and aniline. Furthermore, the introduction of the amino group in the naphthalene ring has had a marked

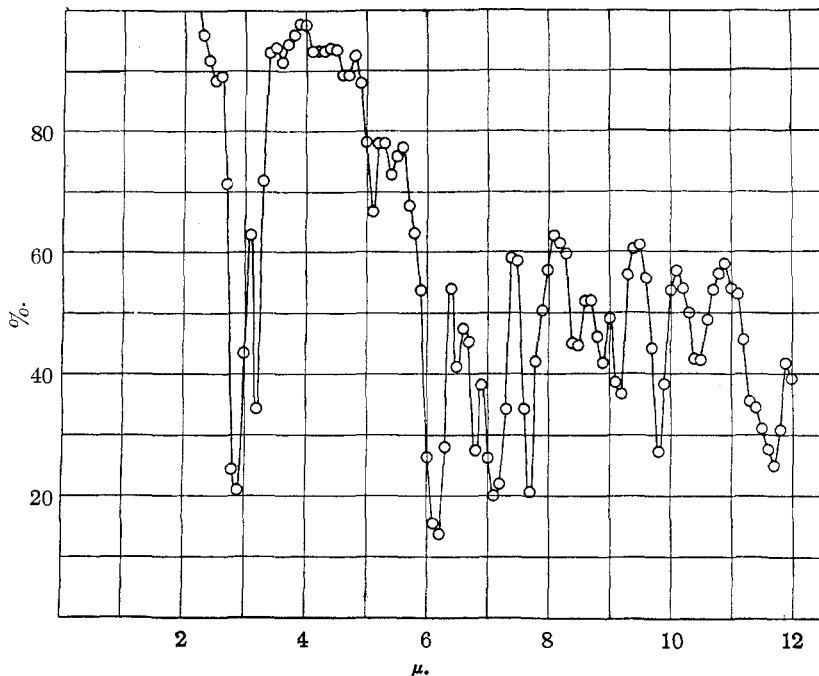


Fig. 1.— α -Naphthylamine; $T = 0.05$ mm. Temp. = 65° .

qualitative effect on the absorption spectrum of naphthalene, again paralleling the case of benzene and aniline.

The 3.25μ band of naphthalene (and benzene) appears at 3.2μ as in the case of aniline. This band is somewhat intensified in passing from benzene to naphthalene and therefore appears considerably deeper for α -naphthylamine than for aniline. The 2.98μ band of ammonia appears at 2.9μ and is deeper than the 3.3μ band.

The curves for the alkyl- α -naphthylamines, shown in Figs. 2 and 3 and for α -naphthylamine reveal a general similarity in the region of the longer wave lengths beyond 4.0μ . In the shorter wave lengths, between 2.8μ and 3.4μ , the absorption spectra are quite analogous to those of aniline and the alkyl anilines. In the methyl- and ethyl- α -naph-

thylamines, the ammonia band at 2.9μ has become shallower than in the case of α -naphthylamine and the 3.2μ band appears at 3.3μ due to the introduction of the methyl group which has a characteristic absorption band at 3.34μ . In the dimethyl and the diethyl derivatives, the 2.8μ ammonia band has practically disappeared and the 3.3μ band has been intensified.

It will thus be seen that the general behavior of these naphthalene derivatives closely parallels that observed in the case of aniline and the alkyl anilines.

Concerning the behavior of the beta isomers, none of these alkyl derivatives have been investigated. However, the absorption spectrum

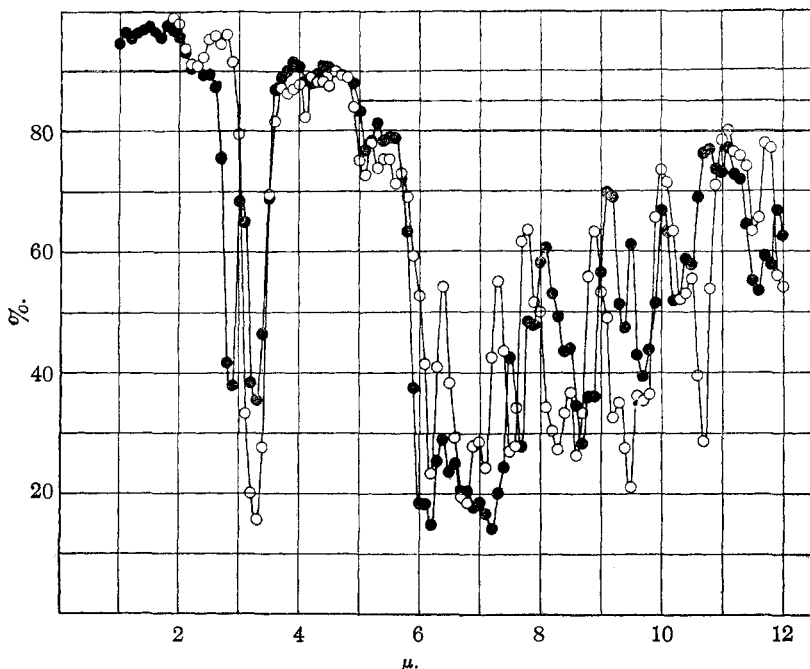


Fig. 2.—Dots, methyl- α -naphthylamine; $T = 0.05$ mm. Circles, dimethyl- α -naphthylamine; $T = 0.05$ mm.

of molten β -naphthylamine at 125° has been examined (this curve has been omitted from the present paper). This seemed especially desirable since Stang's curves show only a slight indication of absorption in the region of 3.0μ . The curve obtained shows a striking similarity to that of the alpha isomer, suggesting the relation that exists between the absorption spectra of *ortho*, *meta* and *para* isomers. The 2.8μ and 3.2μ bands are present and it seems more than probable, therefore, that the absorption of the alkyl β -naphthylamines in this region is analogous to that of the alkyl α -naphthylamines.

The general transparencies of the α - and β -naphthylamines were found to be of the same order of magnitude, so that the high degree of transparency indicated in Stang's curves for β -naphthylamine solutions in carbon tetrachloride and carbon disulfide must be attributed to the low concentration of the solute. He does not state the concentrations of the solutions employed.

The progressive weakening of the ammonia band at 2.98μ with progressive substitution of the three hydrogen atoms of ammonia, yielding first an aryl primary amine, then an aryl-alkyl secondary amine and finally

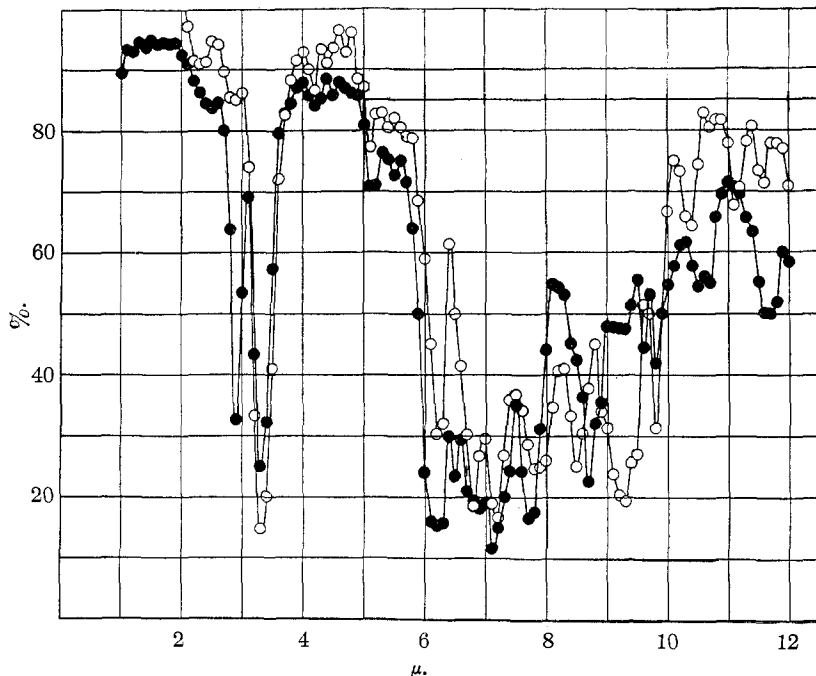


Fig. 3.—Dots, ethyl- α -naphthylamine; $T = 0.05$ mm. Circles, diethyl- α -naphthylamine; $T = 0.05$ mm.

an aryl-dialkyl amine, until it is practically absent in this type of tertiary amine, suggests that there might be another region of absorption of ammonia present in these derivatives which undergoes a similar change.

In this connection, attention is directed to the absorption in the region of 6.2μ as shown in the present curves. Coblentz' curve⁷ for ammonia shows a sharp and deep band at 6.1μ . The transmission at this point was approximately 20%, while that of the 2.98μ band was nearly 75%.

In α -naphthylamine the absorption has a minimum at 6.15μ (also in β -naphthylamine). On introducing one methyl or one ethyl group

⁷ Ref. 1, p. 53.

in the amino group, this band becomes broader and much less sharply defined, the minimum appearing in the region of 6.2μ .

On passing to the dimethyl and diethyl derivatives, this band is quite sharp and appears at 6.2μ for the dimethyl- and at 6.25μ for the diethyl- α -naphthylamine.

An examination of this same region in the case of aniline and the alkyl anilines shows that aniline has a sharp band at 6.1μ . In all of the mono- and dialkyl anilines investigated, this band is sharply resolved at 6.2μ , with the exception of *n*-propylaniline (at 6.15μ), *n*-butylaniline (at 6.1μ) and *iso*-amylaniline (at 6.1μ). It is to be noted that all three of these compounds are secondary amines and that, therefore, in all of the dialkyl anilines (tertiary amines), the band appears consistently at 6.2μ .

The conditions in this region are somewhat complicated as a result of the observation of Coblentz⁸ that the shallow 6.25μ band of benzene is greatly intensified in numerous benzene derivatives which indicates that the vibration in this region is less damped for these derivatives. It appears that this unusual observation also applies in the case of naphthalene and some naphthyl compounds. The author's curve for naphthalene⁹ reveals a shallow but well-defined band at 6.3μ . Stang's measurements for α - and β -naphthol and α -nitronaphthalene show definite absorption in this region.

Concerning this apparent shifting of the 6.1μ band of aniline and α -naphthylamine to 6.2μ in the case of the alkyl anilines and the alkyl α -naphthylamines, the following explanation is suggested.

In the primary amines of this type (aniline and α -naphthylamine), the 6.1μ band of ammonia predominates and practically eliminates any influence of the 6.25μ band. In the mono-alkyl derivatives, the 6.1μ band is weakened and the minimum appears between 6.1 and 6.25μ . The broad band of the monomethyl and the mono-ethyl- α -naphthylamines is regarded as indicating that the 6.1 and the 6.25μ bands now have approximately the same intensity. In the dialkyl derivatives, the 6.1μ band has disappeared and the 6.25μ band appears in its true position.

In contradiction to this suggested explanation, the possibility presents itself that the 6.1μ band of ammonia is entirely absent or negligible in these ammonia derivatives and it is a question of true shifting of the 6.25μ band and that the magnitude of this shifting varies with the number of hydrogen atoms substituted in the amino group.

More data will be necessary to test the validity of these suggestions adequately. An investigation of the alkyl amines, which will be included in future studies of this series, should be of particular interest in this connection, since it is to be expected that the 6.25μ band is absent from these compounds.

⁸ Ref. 1, p. 77.

⁹ Ref. 3, p. 2814.

Summary

1. The infra-red absorption spectra of molten α -naphthylamine at 65°, methyl- and ethyl- α -naphthylamine, and dimethyl- and diethyl- α -naphthylamine have been examined between 1.0 and 12.0 μ .

2. The data obtained indicate a general parallelism with the behavior of aniline and the alkyl anilines previously studied.

3. The marked qualitative differentiation between aniline and mono-alkyl anilines and dialkyl anilines previously found in the region from 2.7 μ to 3.4 μ is apparently valid in the case of α -naphthylamine and its mono- and dialkyl derivatives.

4. The striking similarity in the absorption spectra of α - and β -naphthylamine renders it very probable that the alkyl β -naphthylamines follow this same differentiation.

5. The possibility of another region of absorption displaying a similar differentiation has been suggested for the region of 6.2 μ .

BALTIMORE, MARYLAND

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

THE COMPOSITION OF YELLOW OIL OBTAINED IN THE MANUFACTURE OF *N*-BUTYL ALCOHOL BY FERMENTATION

BY C. S. MARVEL AND A. E. BRODERICK

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"Yellow oil"¹ is the high-boiling material that is produced as a by-product in the fermentation process now used for the preparation of butyl alcohol. In this process a suitable mash, which is made from corn, is inoculated with a pure culture of the Weizmann bacillus and fermented under carefully controlled conditions, optimum for the formation of the solvents. Large quantities of hydrogen and carbon dioxide are produced during the fermentation. The fermented mash is run through a continuous beer-still heated with live steam and the solvents are concentrated in the distillate. This distillate is fractionated in pot stills and the three main products of the fermentation, ethyl alcohol, acetone and butyl alcohol, are separated. The high-boiling residue in the stills amounts to 0.5 to 1.0% of the total yield of solvents and is technically known as yellow oil. It is a dark, amber-colored liquid with the odor of crude butyl alcohol. It usually contains considerable suspended material that may be removed by filtration.

Ethyl alcohol, acetone, butyl alcohol, acetic acid and *n*-butyric acid are well-known products of this fermentation, but there is no report in the

¹ The yellow oil was kindly furnished by Mr. B. K. Brown of the Commercial Solvents Corporation, Terre Haute, Indiana. The authors are greatly indebted to this Company for the aid which has been received in carrying out this investigation.