and of Abel, Schmid and Schafranik[9] for methylamine and ammonia, respectively, using the curve-matching method of Dusenbury and Powell.[6] When all the values were considered, the rates corresponded exactly with the Taylor–Abel third-order rate equation over *p*H 3.5–4.6. The observed rates were somewhat larger than they should have been over *p*H 0.2–2.1, but they were closer to the third order rate law than to any other.

The results can all be reconciled by assuming two mechanisms. One is predominantly that followed in deamination

$$NO^+ + NH_3 \underset{k_b}{\overset{k_a}{\rightleftharpoons}} N_2{-}H_3O^+$$

$$N_2 - H_3O^+ + B^- \xrightarrow{k_c} N_2 + HB + H_2O$$

where B^- is a generalized base. Steady state computation gives

$$\frac{d(N_2)}{dt} = \frac{k_a k_c (NO^+)(NH_3)(B^-)}{k_b + k_c(B^-)}$$

which gives at low (B^-) the Taylor–Able mechanism (when B^- is only NO_2^-) and at high (B^-) the mechanism of Dusenbury and Powell and those cases where chloride or bromide ions are catalysts. The second mechanism involving N_2O_3 appears peculiar to diazotization. However, only where the amine dependence is zero is it kinetically distinguishable from the Taylor–Abel case.

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(9) E. Abel, H. Schmid and J. Schafranik, *Z. physik. Chem.*, *Bodenstein Festband*, 510 (1931).

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Absorption Spectra of Solutions of Pheophytin a in Methanol Containing Acid or Base[1]

BY ROBERT LIVINGSTON, RUDOLPH PARISER, LOU THOMPSON AND ALBERT WELLER

RECEIVED FEBRUARY 28, 1953

In the study of the kinetics of a photosensitized reaction it was necessary to use the extinction coefficients of pheophytin **a** at several different wave lengths and in solutions of varying acidity. Since such data were not available,[2] the absorption spetra of pheophytin **a**, dissolved in methanol containing a wide range of concentrations of added acid or base, were measured.

Experimental Materials and Methods

Pheophytin **a** was prepared as follows: 0.6 ml. of a 2.4 *m* solution of HCl in methanol was added to 150 ml. of a 4 × 10^{-4} *m* solution of purified chlorophyll **a**[3] in ether. After standing for about 6 hours at room temperature, the pheophytin was transferred to about 10 ml. of petroleum ether A, and was purified chromatographically on powdered sugar, using petroleum ether A containing 0.5% isopropyl alcohol as a developer. Only a single band appeared on the column. The absorption spectrum of an ethereal solution of this material agreed closely with the spectrum published by Zscheile and Harris.[4]

Methanolic hydrochloric acid was prepared by bubbling dry hydrogen chloride into purified methanol.[5] Solutions of sodium methoxide were prepared by dissolving clean sodium in purified methanol. The concentrations of these solutions were determined by titration with standard aqueous solutions of acid and base.

The spectrophotometric measurements were made (at approximately 25°) with a Beckman DU spectrophotometer, using 10.0-mm. Corex cells. A few experiments were performed, with a Carey recording spectrophotometer, to test for the possible existence of a transient, reversible form of pheophytin in basic solutions.

Results and Conclusions

Values of log I_0/I of 1.5 × 10^{-5} *m* pheophytin **a**, from λ3400 to 7000 Å., were measured at 100 Å. intervals for methanolic solutions containing the following added substances at the concentrations indicated: (1) 10^{-1} *m* HCl, (2) 10^{-2} *m* HCl, (3) 10^{-3} *m* HCl, (4) 10^{-4} *m* HCl, (5) 3 × 10^{-5} *m* HCl, (6) 10^{-5} *m* HCl, (7) 5 × 10^{-6} *m* HCl, (8) 10^{-6} *m* HCl, (9) 7.5 × 10^{-2} *m* $CH_2Cl{\cdot}COOH$ + 7.5 × 10^{-3} *m* $CH_2Cl{\cdot}COONH_4$, (10) no added substance, (11) 10^{-3} *m* CH_3CONa, and (12) 10^{-1} *m* CH_3CONa. The absorption spectra of solutions (1) and (2) correspond to curve A of Fig. 1; of solutions (8), (9) and (10) to curve N; and of solutions (11) and (12) to curve B.

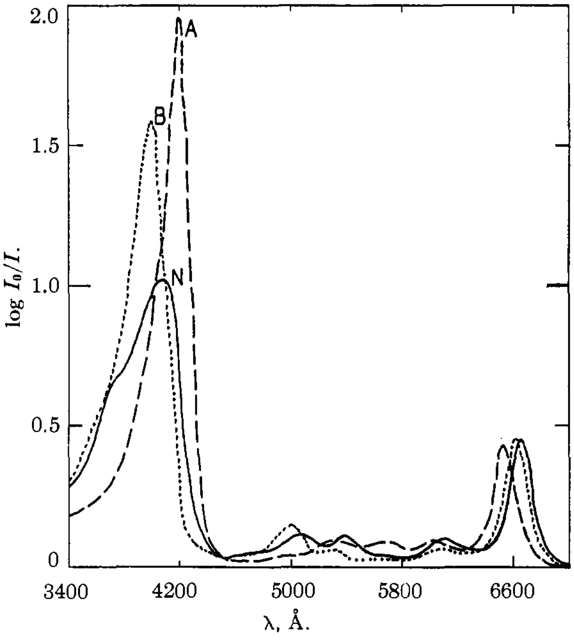

Fig. 1.—Absorption spectra of pheophytin in neutral, acidic and basic methanolic solutions: A, solutions containing HCl at concentrations of 10^{-2} *m* or greater; N, solutions in pure methanol; B, solutions formed by dissolving pheophytin in strongly basic solutions.

TABLE OF PRINCIPAL MAXIMA

Solutions	λ, Å.	log I_0/I	λ, Å.	log I_0/I
A	4180	1.95	6525	0.43
N	4080	1.04	6670	0.45
B	4000	1.57	6630	0.44

The spectra of solutions (3) to (7) exhibit (principal) isobestic points at λ4030 and 6600 Å. Spectra

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[1] This work was made possible by the support of the Office of Naval Research (NR 059,028, Contract N6ori-212, T.O.I) to which the authors are indebted. R. Pariser, Ph.D. Thesis, Univ. of Minnesota, 1950.

[2] Compare, however, W. Broser and W. Lautsch, *Naturwissenschaften*, **38**, 209 (1951).

[3] R. Livingston, D. Sickle and A. Uchiyama, *J. Phys. Chem.*, **51**, 775 (1947).

[4] F. Zscheile and D. Harris, *Bot. Gaz.*, **104**, 515 (1943).

[5] R. Livingston and R. Pariser, THIS JOURNAL, **70**, 1510 (1948).

identical with those observed for these solutions can be obtained by linear combination of curves A and N. The acid form (A) is stable in acid solutions and exists in (rapidly reversible) equilibrium with the neutral form (N) in solutions of intermediate acidity.

In basic solutions pheophytin undergoes an irreversible reaction producing a single substance whose absorption spectrum is represented by curve B. If a basic solution containing this reaction product is neutralized with acid, the absorption spectrum of the resulting solution has its principal maxima at λ4120 and 6480 Å. In dilute solutions of strong base (or of moderate concentrations of aliphatic amines), the irreversible reaction of pheophytin to form the product (B) is measurably slow. There is no evidence for the transient existence, in any of these solutions, of a reversible, intermediate basic form of pheophytin.

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N-Phenylpyrrolidine[1]

BY CARL J. OLSEN AND ARTHUR FURST[2]

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By passing tetrahydrofuran and aniline over activated alumina at 400°, Yur'ev and Minkina[3] obtained N-phenylpyrrolidine in 45.5% yield. Bourns, Embleton and Hansuld,[4] by carefully controlling feed rate, molar ratios and temperature conditions, increased the yield to 88%.

A study was made to see if the desired product could be obtained by merely heating tetrahydrofuran and aniline in an autoclave with a Lewis acid. When aluminum chloride was used as a catalyst N-phenylpyrrolidine was obtained in 42% yield. It was subsequently found possible to obtain a 20% yield in the presence of aluminum chloride at atmospheric pressure.

Experimental

Pressure Reaction.—A mixture of 4.0 g. (0.043 mole) of aniline, 5.7 g. (0.054 mole) of anhydrous aluminum chloride and 4.0 g. (0.056 mole) of tetrahydrofuran was placed in an autoclave, and the pressure was brought up to 1000 lb./sq. in. with nitrogen gas. The mixture was heated to 240° and rocked for 24 hours. The amber colored semi-solid reaction product was made basic with sodium hydroxide solution and extracted with ether. The ether was removed and N-phenylpyrrolidine was recovered by distillation under reduced pressure; b.p. 106–109° (6 mm.), yield 2.7 g. (0.018 mole) or 42.6%, m.p. *ca.* 13°, picrate, m.p. 116–118°, lit. value[3] 116°. No depression of melting point was noted when authentic picrate was mixed with product above.

Other catalysts used and yields were: hydrogen chloride (3.2%), sulfuric acid (no yield), phosphorus pentoxide (31.6%), activated alumina (no yield).

Atmospheric Pressure.—Anhydrous aluminum chloride, 28.5 g. (0.210 mole), was added in portions to 20.0 g. (0.215 mole) of aniline. The temperature rose to *ca.* 150°. With constant stirring, 20.0 g. (0.276 mole) of tetrahydrofuran was added drop by drop. The solution darkened. The temperature was maintained at 150–160° by heating. After one-third of the tetrahydrofuran was added the temperature dropped. The reaction mixture was heated to reflux and the remainder of the tetrahydrofuran added. Refluxing was continued two more hours.

On cooling, the solution was made basic, steam distilled, and the distillate extracted with ether. A yield of 6.1 g. (0.042 mole), 19.8%, N-phenylpyrrolidine was obtained.

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[1] Taken in part from the Master of Science Thesis of Carl J. Olsen, June, 1952.

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[3] Yu. K. Yur'ev and G. A. Minkina, *J. Gen. Chem.* (*USSR*), **1**, 2945 (1937); *C. A.*, **32**, 5399 (1938).

[4] A. N. Bourns, H. W. Embleton and M. K. Hansuld, *Can. J. Chem.*, **30**, 1 (1952).

The Benzoylation of Quinaldine Oxide

BY IRWIN J. PACHTER

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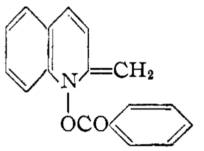
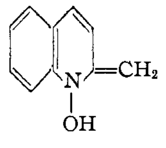
The reaction of quinaldine oxide (I) with benzoyl chloride and sodium hydroxide was investigated by Henze[1] who obtained a compound, $C_{17}H_{13}NO_2$, which was formulated as IIa. Upon treatment with either acid or alkali the compound was converted to a new substance, $C_{10}H_9NO$, isomeric with quinaldine oxide. This substance reacted with Fehling solution and Tollens reagent, but not with phenylhydrazine or hydroxylamine. Structure IIIa was suggested for the debenzoylated product.[1]



IIa



IIIa

A substance of structure IIIa would undergo facile tautomerism to quinaldine oxide, particularly under the conditions employed in effecting debenzoylation. It may therefore be discounted as a possibility. A more likely product would be 2-quinolinemethanol (IIIb) which, being analogous to an α-ketol, would be expected to undergo oxidation in Fehling solution and Tollens reagent. A reaction scheme for the formation of IIIb, involving attack of hydroxyl ion or water on the methylene group of IIa with concurrent elimination of benzoate ion or benzoic acid, can readily be formulated.

The syntheses described by Henze were repeated. The identity of the debenzoylated product with a sample of 2-quinolinemethanol prepared from methyl quinaldate by reduction with lithium aluminum hydride[2,3] was established by mixture melting point determination and infrared spectroscopy.

The infrared spectrum of the compound formulated as IIa was examined. The absence of bands indicative of a terminal methylene group suggested that the product might be 2-quinolinemethyl benzoate (IIb). To test this possibility, IIIb was rebenzoylated. The compound thus obtained was

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[1] M. Henze, *Ber.*, **69**, 534 (1936).

[2] C. E. Kaslow and W. R. Clark, *J. Org. Chem.*, **18**, 55 (1953).

[3] The author is grateful to Professor C. E. Kaslow for supplying this authentic sample.