542 mg. (47%); m.p. 150°. An analysis by long digestion with $CaCl_2$ at 70° (equation: $3Ca^{++} + 2H_2OBF_3 + 2H_2O \rightarrow 3CaF_2 + 6H^+ + 2HBO_2$) gave 2.93 m.e. of H^+ and 1.06 m.e. of HBO_2 per m.e. of $(CH_3)_3POBF_3$.

These results suggest that $(CH_3)_3POBF_3$ is slightly more stable than H_2OBF_3, although the latter preponderates, in ionized form, when there is a great excess of water.

The Compound $(CH_3)_3POSO_3$.—The preparation of $(CH_3)_3POSO_3$ was done first by the use of the double U-tube system: SO_3 was evaporated from the first U-tube and carried by a stream of nitrogen over $(CH_3)_3PO$ in the second. The sample was kept at room temperature or lower, since a working temperature of 70° led to charring. After considerable absorption had occurred, liquid SO_3 was three times condensed upon and evaporated from the solid; finally the excess SO_3 was carried off by the nitrogen stream, while the product was gradually heated to 140°. The gain in weight then corresponded to 1.05 SO_3 per $(CH_3)_3PO$. The white solid product, very reactive toward water, melted with irreversible decomposition, in the range 180–200°. Vacuum sublimation proved impossible.

In an attempt to purify this product, a sample was dissolved in anhydrous ethanol, and ether was added to precipitate a solid which melted at 87–88°. Analyses gave 27.15% C, 6.46% H, and 20.18% ethoxy-groups,[9] corresponding to another new compound, $(CH_3)_3POH^+OSO_3C_2H_5^-$ (calcd. C, 27.51; H, 6.94, and C_2H_5O, 20.20). This alcoholysis indicates a weaker bonding of $(CH_3)_3PO$ to SO_3 than that in $(C_2H_5)_3NOSO_3$, which could be washed with cold ethanol without reaction.[5]

A better sample of $(CH_3)_3POSO_3$ was prepared by leading sulfur trioxide over a solution of 300 mg. of $(CH_3)_3PO$ in 2 ml. of 1,2-dichloroethane, again in the double U-tube system, with care to avoid an excess of SO_3. The precipitate was washed with fresh solvent and dried in high-vacuum at 35°. Again the melting involved decomposition (165–200°). *Anal.*[9] C,20.32; H, 5.40 (calcd. 20.93 and 5.27; deviations attributable to 3% absorption of moisture). The rapid destruction of this substance by water was shown by the drop in *p*H from 6.9 to 2.1 within 5 seconds after formation of a 0.1% solution. The $BaCl_2$ test for sulfate also was immediate, and an electrometric titration showed the expected quantity of acid.

The Behavior of $(CH_3)_3PO$ **toward** SO_2.—In sharp contrast to the vigorous process of formation and strong bonding of $(CH_3)_3NOSO_2$,[2] trimethylphosphine oxide smoothly absorbs SO_2 to form a liquid with a saturation limit of about 50 mole per cent. $(CH_3)_3PO$. The saturation pressure of SO_2 over this liquid is scarcely one-tenth that expected in terms of Raoult's law; hence some kind of weak combination is indicated. A series of pressure–composition isotherms at −23, 0, 8 and 18°, for the system $(CH_3)_3PO–SO_2$, showed a virtually constant pressure at each temperature until all of the solid had dissolved; then the pressure rose very sharply and almost linearly with increasing SO_2 content. These results are summarized in Table I, in which P_s refers to the pressure of SO_2 in equilibrium with the saturated liquid and x_s is the molar ratio of SO_2 to $(CH_3)_3PO$ at the saturation point. *S*, the slope of the pressure–composition graph beyond the level region, is expressed as mm. change of pressure per unit change of the ratio of SO_2 to $(CH_3)_3PO$.

The values of p_s at the four temperatures determine the equation $\log_{10} p = 6.592 - 1325/T$, from which the check values were computed. Such linearity would be expected if the saturated liquid were assumed to represent a single compound such as $(CH_3)_3POSO_2$, but the evidence is not sufficient for this specific interpretation.

TABLE I

PRESSURE–COMPOSITION ISOTHERMS FOR $(CH_3)_3PO–SO_2$

t, °C.	p_s (mm.) (obsd.)	p_s (mm.) (calcd.)	x_s	*S*
−23	19.2	19.4	1.10	61
0	54.5	54.1	1.05	216
8	76.6	74.5	0.98	244
18	106.5	108	0.92	278

LOS ANGELES 7, CALIFORNIA RECEIVED MAY 14, 1951

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[9] Analyses by Joseph Pirie, of this Department.

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF THE UNIVERSITY OF KANSAS]

Further Observations on Reissert Compounds

BY WILLIAM E. MCEWEN, J. VERNON KINDALL, ROBERT N. HAZLETT AND ROBERT H. GLAZIER

The yellow compound obtained in the reaction of 2-benzoyl-1,2-dihydroisoquinaldonitrile (I) with hydrochloric acid has been investigated. On the basis of a molecular weight determination, the ultraviolet and visible spectra, the hydrolysis products, the oxidation products, and by analogy with other known substances, the compound is assigned the structure VII, 2-(1′-isoquinolyl)-4,5-diphenyloxazole. Evidence is offered regarding the mechanism by which it is formed. A rearrangement affording 2-quinolylphenylmethylcarbinol (XI) from a reaction of 1-benzoyl-1,2-dihydroquinaldonitrile (VIII) with methylmagnesium bromide is also discussed.

Some time ago a mechanism was proposed for the acid-catalyzed formation of aldehydes from Reissert compounds, and evidence in support of that mechanism was presented.[1] Mention was also made of the isolation of a yellow compound of unknown structure, together with benzaldehyde, isoquinaldic acid, benzoin and benzoin isoquinaldate (V), on reaction of 2-benzoyl-1,2-dihydroisoquinaldonitrile (I) with concentrated hydrochloric acid. The yellow compound had previously been reported by Reissert, who assigned the molecular formula $C_{34}H_{23}N_3O$, on the basis of the analysis for its elements.[2]

We have now determined that the yellow compound is 2-(1′-isoquinolyl)-4,5-diphenyloxazole (VII) on the basis of the following facts: (1) It is not possible to distinguish between the molecular formulas $C_{34}H_{23}N_3O$ and $C_{24}H_{16}N_2O$ by combustion analyses.[3] (2) A molecular weight determination by the Rast method gave a value of 353, as compared to a theoretical value of 348 for a compound of the molecular formula $C_{24}H_{16}N_2O$. (3) The conventional tests of qualitative organic analysis indicate the absence of carbonyl-containing cyano, hydroxyl or primary or secondary amino groups. (4) The ultraviolet and visible absorption spectrum (Fig. 1) shows a maximum at 410 mμ, which is reasonable for a compound having several aromatic rings in conjugation with one another. (5) The compound is very resistant to hydrolysis under both acid and alkaline conditions, but a 6% yield of benzoin and a 5% yield of isoquinaldic acid, together with an 85% recovery of starting

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[1] W. E. McEwen and R. N. Hazlett, THIS JOURNAL, **71**, 1949 (1949).

[2] A. Reissert, *Ber.*, **38**, 3415 (1905).

[3] *Anal.* Calcd. for $C_{34}H_{23}N_3O$: C, 83.39; H, 4.73; N, 8.61. *Anal.* Calcd. for $C_{24}H_{16}N_2O$: C, 82.73; H, 4.63; N, 8.04.

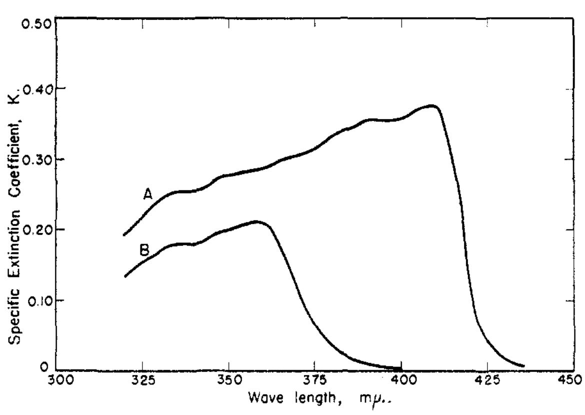
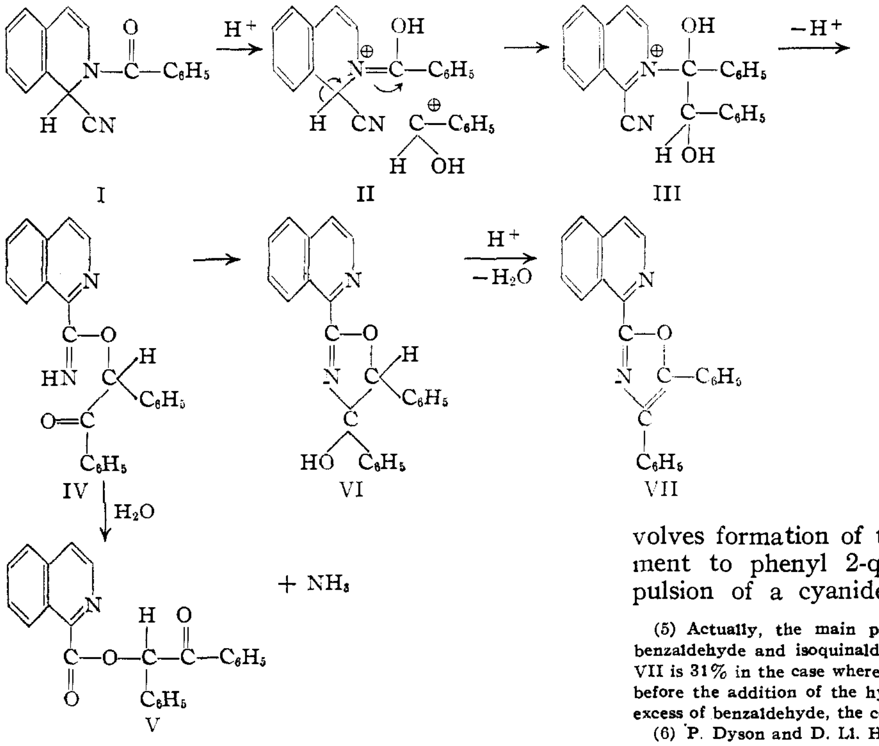


Fig. 1.—Absorption spectra in ethanol of: (A) 2-(1'-isoquinolyl)-4,5-diphenyloxazole (VII); (B) 2-benzoyl-1,2-dihydroisoquinaldonitrile (I).

material, was obtained after one week of refluxing in 25% sulfuric acid solution. (6) The results of a potassium permanganate oxidation in pyridine solution imply that two moles of benzoic acid are formed per mole of the yellow compound oxidized. (7) It is known that benzoin and benzonitrile combine to give 2,4,5-triphenyloxazole in a reaction catalyzed by concentrated sulfuric acid.[4] This combination of reagents is somewhat analogous to the mixture of compounds formed in the acid-catalyzed reaction of the isoquinoline Reissert compound, but isoquinaldonitrile does not combine with benzoin to give VII in sulfuric acid solution.



In addition to the facts previously presented in support of the mechanism proposed for the acid-catalyzed formation of aldehydes from Reissert compounds,[1] the following additional points must be taken into consideration in offering an explanation for the formation of the 2-(1'-isoquinolyl)-4,5-diphenyloxazole (VII): (1) The addition of an excess of benzoin to the 2-benzoyl-1,2-dihydroisoquinaldonitrile (I) prior to reaction with the concentrated hydrochloric acid does not increase the yield of VII. (2) Isoquinaldonitrile does not react with benzoin to give VII under the same conditions employed in its preparation from I. (3) The yield of VII is markedly increased by the addition of an excess of benzaldehyde to I prior to the reaction with hydrochloric acid.[5]

A mechanism for the formation of VII, consistent with the known facts, consists of the formation of the conjugate acid (II) of I, reaction of this with the conjugate acid of benzaldehyde to give the complex, III, which then affords the imino-ether, IV, by an intramolecular rearrangement. All of this is identical with the mechanism previously proposed for the reaction of the quinoline Reissert compound with benzaldehyde and hydrochloric acid.[1] The imino ether, IV, then undergoes either a hydrolysis to benzoin isoquinaldate (V) or a cyclization to the hydroxydihydro-oxazole (VI). In a simple acid-catalyzed dehydration, VI affords 2-(1'-isoquinolyl)-4,5-diphenyloxazole (VII).

Another interesting rearrangement involving a Reissert compound was uncovered in a reaction of 1-benzoyl-1,2-dihydroquinaldonitrile (VIII) with methylmagnesium bromide. Methylphenyl-2-quinolylcarbinol (XI), identical with a sample obtained by means of a Hammick reaction involving quinaldic acid and acetophenone,[6] was obtained in about 50% crude yield. A similar rearrangement failed to occur on reaction of phenylmagnesium bromide or mesitylmagnesium bromide with VIII. Only traces of amine fractions were obtained, but the remaining details of these reactions have not been worked out as yet. The failure of the aryl Grignard reagents to bring about the rearrangement might be due to their greater size or their lesser tendency to attack the α-hydrogen atom in reaction with a nitrile.[7]

The reaction probably involves formation of the anion, IX,[8] its rearrangement to phenyl 2-quinolyl ketone (X) by expulsion of a cyanide ion,[9] and finally, reaction

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[4] F. R. Japp and T. S. Murray, *J. Chem. Soc.*, 63, 469 (1893).

[5] Actually, the main products formed in these reactions are benzaldehyde and isoquinaldic acid. The combined yield of V and VII is 31% in the case where an excess of benzaldehyde is added to I before the addition of the hydrochloric acid. In the absence of an excess of benzaldehyde, the combined yield is about 12%.

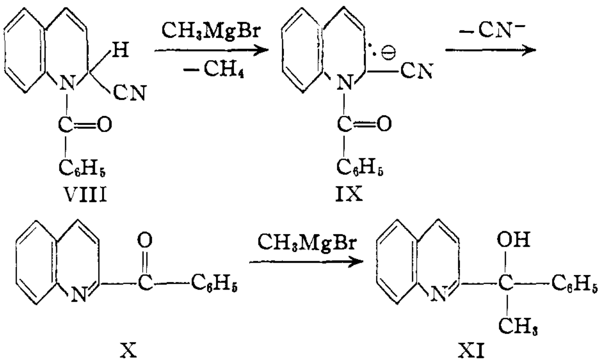
[6] P. Dyson and D. Ll. Hammick, *J. Chem. Soc.*, 1724 (1937).

[7] C. R. Hauser and W. J. Humphlet, *J. Org. Chem.*, 15, 359 (1950).

[8] Structure IX represents only one of many contributing resonance structures.

[9] V. Boekelheide and J. Weinstock (Abstracts of Papers Presented at Boston, Mass., April 2 to 5, 1951) have independently and essentially simultaneously discovered the same rearrangement. They converted VIII to X by means of sodium hydride, sodium cyanide being produced as a by-product.

of X with methylmagnesium bromide to give XI.



An attempted Stephens reduction of VIII failed to yield the anticipated quinoline-2-aldehyde. A reaction of VIII with dry hydrogen chloride in dry ether solution afforded a precipitate, the neutral hydrolysis of which provided a 45% yield of quinaldamide.

Experimental[10]

2-Benzoyl-1,2-dihydroisoquinaldonitrile (I).—Prepared by the method of Padbury and Lindwall.[11]

Reaction of 2-Benzoyl-1,2-dihydroisoquinaldonitrile (I), Benzaldehyde and Hydrochloric Acid.—From 10.0 g. of I, 15.0 g. of benzaldehyde and 50 cc. of concentrated hydrochloric acid, there was obtained 1.34 g. (9.5%) of benzoin isoquinaldate, m.p. 152.8–153.0°, 2.88 g. (21.5%) of 2-(1′-isoquinolyl)-4,5-diphenyloxazole (VII), m.p. 124–125° and 0.30 g. (4%) of benzoin.[1]

Reaction of 2-Benzoyl-1,2-dihydroisoquinaldonitrile (I) with Hydrochloric Acid.—To 10.00 g. of I was added 50 cc. of concentrated hydrochloric acid with mechanical stirring, in the course of 45 minutes. The stirring was continued another two hours, and then the mixture was allowed to stand for 20 hours. The mixture was made neutral by addition of 10% sodium hydroxide solution, then steam-distilled until all the benzaldehyde had been removed. The residual solution was made basic by addition of sodium hydroxide solution, and a red insoluble oil was taken up in ether, dried over anhydrous sodium sulfate and treated with decolorizing charcoal. Evaporation of the ether afforded 1.43 g. of yellow-brown solid, m.p. 83–115°. Since the components of this mixture have been reported previously,[1,2] no further attempt at purification of the mixture was made.

Reaction of 2-Benzoyl-1,2-dihydroisoquinaldonitrile (I), Benzoin and Hydrochloric Acid.—To 10.00 g. of I, intimately mixed with 10.00 g. of benzoin, was added 50 cc. of concentrated hydrochloric acid with mechanical stirring in the course of 45 minutes. The stirring was continued another two hours, and then the mixture was allowed to stand for 20 hours. The mixture was diluted by addition of 100 cc. of water and extracted with 500 cc. of ether. An orange solid, insoluble in either layer, was filtered off. A combination of extraction procedures, using 25% hydrochloric acid and benzene, and a fractional crystallization of the basic fraction, from ethanol, afforded the following substances from the orange solid: 0.60 g. of benzoin isoquinaldate (V), m.p. 152–153°; 0.70 g. of 2-(1′-isoquinolyl)-4,5-diphenyloxazole (VII), m.p. 124–125°; 0.41 g. of isoquinaldamide, m.p. 170–171° (reported,[2] m.p. 168–169°); and 0.30 g. of an impure amine, m.p. 157–175°. The known substances above, on mixed m.p. determinations with authentic samples, showed no depressions.

From the ether and benzene extracts and also from the fractional crystallization, there was recovered 9.35 g. of benzoin. About 1.0 g. of gummy material remained after the various separation procedures had been carried out, and this resisted further purification.

Properties of 2-(1′-Isoquinolyl)-4,5-diphenyloxazole (VII).—The substance forms insoluble salts with dilute hydrochloric and sulfuric acids, the hydrochloride decomposing at 192–195° and the sulfate at 212–215°. The base is soluble in ethanol at room temperature to the extent of about 2 g./l. The substance does not absorb hydrogen at one atmosphere pressure over Adams catalyst at room temperature.

Isoquinaldonitrile.—Prepared from I by the method of Kaufmann and Dandliker.[12]

Reaction of Isoquinaldonitrile, Benzoin and Hydrochloric Acid.—A mixture of 0.70 g. of isoquinaldonitrile, 0.97 g. of benzoin and 30 cc. of concentrated hydrochloric acid was allowed to stand at room temperature for 20 hours. The mixture was diluted to 125 cc. and filtered, 0.93 g. (96%) of the benzoin being recovered unchanged.

Hydrolysis of 2-(1′-Isoquinolyl)-4,5-diphenyloxazole (VII).—To 40 cc. of 25% sulfuric acid solution was added 2.00 g. of VII, and the mixture of yellow solid and solution was refluxed for one week. Some solid material which had steam-distilled into the condenser was washed down with water, and the mixture was extracted with ether. Some solid remained undissolved in either layer. The ether solution was washed with sodium bicarbonate solution (no organic acid obtained on acidification), then dried over anhydrous sodium sulfate. Evaporation of the ether afforded 0.07 g. (6%) of benzoin, m.p. 132–134° after one crystallization from ethanol. A mixed m.p. with an authentic sample of benzoin showed no depression.

The acid layer containing the yellow solid was made basic with sodium hydroxide solution. The mixture of solid and solution was extracted with ether, the solid dissolving in the ether. Evaporation of the ether, dried over anhydrous sodium sulfate, gave 1.70 g. (85%) of the starting material, m.p. 124–125° after one crystallization from ethanol.

The alkaline solution was made faintly acid with acetic acid. Addition of a saturated solution of copper acetate with heating on the steam-bath caused a blue-green precipitate to form. This was filtered, washed with distilled water and then decomposed by means of hydrogen sulfide. The copper sulfide was filtered and washed with hot water. Evaporation of the combined filtrate and wash afforded 0.05 g. (5%) of isoquinaldic acid, m.p. 161–162° (dec.), also in admixture with an authentic sample of isoquinaldic acid.

Oxidation of 2-(1′-Isoquinolyl)-4,5-diphenyloxazole (VII).—A solution of 0.25 g. of VII and 0.60 g. of potassium permanganate in 20 cc. of 50% pyridine was refluxed until the purple color disappeared. Three additional 0.30-g. portions of potassium permanganate were added, each time with refluxing until the purple color was gone. The mixture was treated with sodium bisulfite to reduce the manganese dioxide present, then made distinctly alkaline with 10% sodium hydroxide solution. Ether extraction of the alkaline solution gave no product other than pyridine. The alkaline solution was made acid with 10% hydrochloric acid solution and then extracted with ether. Evaporation of the ether afforded 0.09 g. of benzoic acid, m.p. 121–122° after one crystallization from water. A mixed m.p. with an authentic sample of benzoic acid showed no depression.

Reaction of 1-Benzoyl-1,2-dihydroquinaldonitrile (VIII) with Methylmagnesium Bromide.—To 20.00 g. of VIII, prepared by the method of Rupe, Paltzer and Engel,[13] in 150 cc. of dry dioxane was added 53 cc. of 4 *M* methylmagnesium bromide in ether in the course of five minutes, with efficient mechanical stirring, the mixture turning a deep red color. The reaction was carried out in a nitrogen atmosphere. The thick mixture was allowed to stand overnight, then the ether and dioxane were distilled *in vacuo*. The residual brown cake was hydrolyzed with 40 cc. of saturated ammonium chloride solution. Then 100 cc. of 2% hydrochloric acid solution was added and the mixture extracted with ether. The aqueous layer was neutralized with sodium bicarbonate solution and again extracted with ether. The combined ether solution was extracted with 5% hydrochloric acid. On making the acid extract basic with 10% sodium hydroxide solution, a brown solid precipitated, was filtered and washed with water, 9.5 g. After treatment with decolorizing charcoal and two crystallizations from ethanol, 6.0 g. of pure methylphenyl-2-quinolylcarbinol (XI), m.p. 101–102°, was obtained.

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[10] Analyses by Oakwold Laboratories, Alexandria, Va. All m.p.'s are corrected.

[11] J. J. Padbury and H. G. Lindwall, THIS JOURNAL, **67**, 1268 (1945).

[12] A. Kaufmann and P. Dandliker, *Ber.*, **46**, 2924 (1913).

[13] H. Rupe, R. Paltzer and K. Engel, *Helv. Chim. Acta*, **20**, 209 (1937).

Anal. Calcd. for $C_{17}H_{15}NO$: C, 81.90; H, 6.07; N, 5.62. Found: C, 81.90, 82.02; H, 6.06, 6.24; N, 5.83, 6.20.

A mixed m.p. with an authentic sample of XI, prepared by the method of Dyson and Hammick,[6] showed no depression.

Similar results were obtained in the reaction of VIII with methylmagnesium bromide in benzene solution.

Preparation of Quinaldamide from VIII.—To 200 cc. of dry ether saturated with hydrogen chloride was added 10.00 g. of VIII. The mixture was mechanically stirred as hydrogen chloride was passed in for 90 minutes. A yellow precipitate which formed was filtered. After boiling the yellow solid in water for a few minutes, 3.0 g. (45%) of quinaldamide, m.p. 131–133°, was obtained.

Anal. Calcd. for $C_{10}H_8N_2O$: C, 69.75; H, 4.68; N, 16.27. Found: C, 69.73; H, 4.65; N, 16.25.

A mixed m.p. with an authentic sample of quinaldamide showed no depression.

LAWRENCE, KANSAS RECEIVED FEBRUARY 19, 1951

[CONTRIBUTION FROM NATIONAL DAIRY RESEARCH LABORATORIES, INC.]

A Study on the Reaction of Aldoses and Amino Acids

BY G. HAUGAARD, L. TUMERMAN AND H. SILVESTRI

A new technique has been developed for the study of the reaction between aldoses and amino acids. The method has been applied to the evaluation of the reaction constants for the formation and degradation of Schiff base produced in various amino acid aldose systems under alkaline conditions. The effect of *p*H on the reaction has been studied and results indicate that its influence on the ionization of the amino acid is reflected in the extent of the reaction. The effect of temperature on the reaction has been studied and the activation energy for the primary reaction of *dl*-leucine and glucose was calculated to be 19,700 calories. Lactose and valine were found to react in equimolar proportions by an adaptation of the new technique. The specific rotation of the Schiff base produced by the reaction of *l*-leucine and gluose was found to be $[\alpha]^{20}\text{D}$ −42.6°. The relationship between the degradation of the Schiff base and the formation of a brown-colored substance is discussed. A kinetic study is presented which supports the theory that the "Browning" reaction involves condensation of amino acids with carbohydrate degradation products.

Introduction

The mechanism of the reaction between amino acids and aldose sugars has been the subject of rather extensive investigations since the original observations were published by L. C. Maillard.[1]

The possible physiological significance of amino acid–aldose interaction as well as the implication of the reaction in deteriorative changes and flavor development in foods have served to stimulate much of the recent research in this field.

A great deal of the literature concerning the reaction rate and mechanism is contradictory, a situation resulting from varying conditions of temperature, hydrogen ion and reactant concentration employed by the various investigators. In most instances the true reaction of amino acid and aldose has been obscured by secondary changes induced in either the amino acid or the aldose by elevated temperatures, and *p*H conditions far removed from neutral.

H. von Euler, *et al.*,[2] and Englis and Dykins[3] attempted to follow the course of the reaction polarimetrically. Using a cryoscopic technique, von Euler, *et al.*,[4] later attempted to demonstrate reaction between glucose and glycine and to check the results by determination of free amino nitrogen and decrease in reducing sugar. An attempt was made by Watanabe[5] to determine the course of reaction of various amino acids and sugars in 0.5 *N* sodium hydroxide, under which highly alkaline conditions quite extensive rearrangements and degradation of the carbohydrate obscured the true picture of the initial reaction.

Frankel and Katchalsky[6,7,8] published a series of papers describing the application of a potentiometric method based on the increase in acidity resulting from the formation of a Schiff base by the reaction of the aldehyde group of the reducing sugar with the amino group of the amino acid. α-Amino nitrogen decrease was determined by the van Slyke technique and data were presented to substantiate the results obtained by the potentiometric method.

Englis and Dykins[3] parallel with a polarimetric study, attempted to substantiate their findings by determination of the expected loss of α-amino nitrogen by the van Slyke nitrous acid technique, but contrary to Frankel and Katchalsky, failed to obtain any decrease even in solutions where marked sugar rotation changes were noted. They attributed this to an equilibrium reversal during the time interval required for the amino nitrogen determination. The work of Englis and Dykins was confirmed in our laboratory.

A new method has been developed, therefore, in order to circumvent the difficulties mentioned. The method is based upon changes in soluble nitrogen in an aldose solution saturated with an amino acid and equilibrated with an excess of amino acid crystals. The necessity of using a physical property, such as solubility, in order to evaluate the kinetics of a reaction of this type is dictated by the rapidity with which the reaction product dissociates into the reactants or forms other products under chemical analysis. This technique—the solubility technique—has also been used to determine the stoichiometry of an aldose–amino acid system, as well as for the determination of the specific rotation of the unstable Schiff base formed.

The following kinetic treatment of this reaction is based upon experimental evidence that aldoses

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(1) L. C. Maillard, *Compt. rend.*, **154**, 66 (1912); **155**, 1554 (1912).

(2) H. von Euler, E. Brunius and K. Josephson, *J. Physiol. Chem.*, **153**, 1 (1926).

(3) D. T. Englis and F. A. Dykins, *Ind. Eng. Chem., Anal. Ed.*, **3**, 17 (1931).

(4) H. von Euler, E. Brunius and K. Josephson, *J. Physiol. Chem.*, **155**, 259 (1926).

(5) J. Watanabe, *J. Biochem. (Japan)*, **16**, 153 (1932).

(6) A. Katchalsky, *Biochem. J.*, **35**, 1024 (1941).

(7) M. Frankel and A. Katchalsky, *ibid.*, **35**, 1024 (1941).

(8) M. Frankel and A. Katchalsky, *ibid.*, **35**, 1034 (1941).