

the diazonium salt (as judged by the rate of gas evolution) is apparently slow.

Experimental

Tetrazole by the Deamination of 5-Aminotetrazole.—A solution of 69.0 g. (1.0 mole) of sodium nitrite in 200 ml. of water was added with vigorous agitation to a slurry consisting of 103.0 g. (1.0 mole) of 5-aminotetrazole monohydrate, 145 g. (1.1 moles) of 50% hypophosphorous acid and 500 ml. of water in a 1500 ml. beaker. The temperature was first allowed to rise to about 35°, after which it was maintained in the range 33–36° by external cooling with an ice-water-bath; the time required for the addition of the nitrite was 25 to 30 minutes. The cooling bath was finally replaced by a water-bath at 35° and the stirring continued for 30 minutes more in order to complete the reaction. The pale-yellow colored solution was cooled to 25°, adjusted to pH 3.4–3.6 (pH meter) with 50% sodium hydroxide solution, and vacuum evaporated on the steam-bath at water-pump pressure to incipient crystallization. The somewhat sirupy residue was refluxed for 10–15 minutes with 500 ml. of 50–50 acetone–ethanol, after which the supernatant liquid was decanted from the insoluble gum. This extraction by refluxing and decanting was repeated with one 250-ml. portion, and four 100-ml. portions of the same mixed solvent. The combined extracts were evaporated to dryness on the steam-bath and the residue of very impure tetrazole was re-extracted with the following portions of boiling ethyl acetate: one 375 ml., one 125 ml. and four 60 ml. Any insoluble gum was discarded. Evaporation of the combined ethyl acetate solutions yielded 65 g. (92.6%) of tetrazole melting at 140–150°. The crude tetrazole was dissolved in 125 ml. of hot glacial acetic acid, cooled to 15°, and filtered. The crystalline product was washed with 25 ml. of cold acetic acid and then with two 50-ml. portions of diethyl ether. The yield of dried product was 43.3 g., m.p. 156–158° (cor.); Mehina and Herbst⁴ reported 157.5–158°. By evaporating the combined mother liquors and washings to 65 ml., cooling, filtering and washing with cold diethyl ether–acetic acid (2:1), there was recovered 11.0 g. more of tetrazole, melting 156–158°. The total recovery amounted to 54.3 g., or 77.6% based on the 5-aminotetrazole.

Anal. Calcd. for CH₂N₄: eq. wt., 70.06. Found: eq. wt., 70.9.

In the remaining acetic acid recrystallization mother liquors there is some kind of phosphorus-containing compound but it was never isolated in pure form for identification and analyses.

Tetrazole and Sodium 5-Chlorotetrazole.—A slurry consisting of 19.4 g. (0.188 mole) of 5-aminotetrazole monohydrate, 80 ml. of 20% sodium hydroxide solution, 56.8 ml. of 20% sodium nitrite solution and 120 g. of crushed ice was added all at once with stirring to a freshly prepared slurry of crushed ice (400 g.), concentrated hydrochloric acid (68 ml.) and 200 ml. of cold H₂O. The temperature held at –2.5 to –3°. After the mixture had been stirred for ten minutes, 28 g. (0.215 mole) of 50% hypophosphorous acid was added. Evolution of gas began immediately. During the two hours allowed for the reduction of the diazonium compound, the temperature was gradually raised to 20°. The solution was adjusted to pH 2.5 with sodium hydroxide solution and then evaporated to dryness under reduced pressure. The residue was extracted with one 200-ml. and four 50-ml. portions of boiling 50–50 ethanol–acetone mixture. Evaporation of the combined extracts left 26.5 g. of material. When the latter was extracted with one 100-ml. and four 50-ml. portions of hot ethyl acetate and the extracts evaporated, there was recovered 5.6 g. (42.6%) of crude tetrazole, m.p. 148–156°, softening 130–135°. In duplicate experiments the yields varied from 26 to 46%.

The ethyl acetate insoluble material was dissolved in 35 ml. of hot water, filtered and allowed to cool slowly. There was recovered 5.4 g. (18.7%) of sodium 5-chlorotetrazole, as the 1.5 hydrate, which decomposed explosively at about 253–255° (depends on the heating rate).

Anal. Calcd. for CN₄ClNa·1.5 H₂O: C, 7.82; H, 1.97; N, 36.49; Cl, 23.10; Na, 14.98. Found: C, 7.92; H, 2.03; N, 36.56; Cl, 22.39; Na, 14.07.

5-Chlorotetrazole was isolated from its sodium salt by precipitation as the copper salt and treatment of the latter

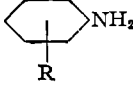
with hydrogen sulfide. The unpurified chlorotetrazole melted at 72–73°, Stolle reported 73°; the measured equivalent weight was 105.7 versus the theoretical 104.51.

Evaporation of the aqueous mother liquors, from which the sodium 5-chlorotetrazole had been removed, left a material which was almost completely soluble in absolute ethanol and which contained phosphorus, but which even after repeated recrystallization, could not be obtained in a sufficiently pure state for satisfactory and meaningful analyses.

Triazole by the Deamination of 3-Amino-1,2,4-triazole.—A solution of 35.0 g. (0.5 mole) of sodium nitrite in 100 ml. of water was added with agitation during 30 minutes to a solution consisting of 42.0 g. (0.5 mole) of 3-amino-1,2,4-triazole, 72.5 g. (0.55 mole) of 50% hypophosphorous acid, 40 ml. of concentrated hydrochloric acid and 250 ml. of water. The temperature was maintained at 35–38°. There was a steady evolution of gas during this period. After the reaction mixture had stood for an additional 30 minutes at 35°, the pH was adjusted to neutral with a 50% solution of sodium hydroxide. The solution was then evaporated to dryness under reduced pressure and the residue extracted with seven 100-ml. portions of boiling ethyl acetate. Evaporation of the ethyl acetate left 26.0 g. (75.3%) of crude 1,2,4-triazole, m.p. 110–120°. The product was best purified by vacuum distillation, followed by one recrystallization from ethyl acetate; long white needles, m.p. 120.5–121° (Pellizzari and Cuneo¹⁰ reported 121°).

Deamination of Substituted Anilines.—A slurry consisting of 0.1 mole of the aniline, 17.0 ml. of concentrated hydrochloric acid and 100 ml. of water was heated to boiling, cooled rapidly to 35° with stirring, treated first with 14.5 g. of 50% hypophosphorous acid, and then during 30 minutes with 6.9 g. (0.1 mole) of sodium nitrite in 20 ml. of water. The temperature was maintained at 30–35°. After one more hour the gas evolution had ceased and the solution no longer gave a positive nitrite test. If the product was volatile in steam, the reaction mixture was adjusted to pH 9–10 with a 50% solution of sodium hydroxide and steam distilled. The distillate was then acidified and steam distilled again. The product was separated from the distillate by conventional means. The benzoic acid which resulted from the deamination of the aminobenzoic acids was filtered from the acid reaction mixture after the latter had been cooled overnight at 5°. The crude product was recrystallized from water. Results are summarized in Table I.

TABLE I

DEAMINATION OF SUBSTITUTED ANILINES					
					
R	2-NO ₂	4-NO ₂	2-COOH	4-COOH	4-C ₆ H ₅
Yield of					
C ₆ H ₅ , %	79	17	64 ^a	31 ^b	33 ^c

^a The melting point of this once recrystallized material was 116–119°, eq. wt. 124.3 (theory 122.1). ^b The melting point of this once recrystallized material was 110–118°, eq. wt. 124.6. ^c The melting point was 68.5–69.5° (reported, 69–70° for diphenyl).

(10) G. Pellizzari and G. Cuneo, *Gazz. chim. ital.*, **24**, I, 510 (1894).

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The Solubility of Potassium Chromate in Aqueous Ethanol Solutions at 25°

By WILLIAM F. LINKE

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Ethanol–water solutions were prepared by measuring appropriate amounts of each liquid with calibrated burets (or pipets). The solvent compositions were thus known to at least one part per thousand. C.P. K₂CrO₄ was added, and the mixtures were stirred by rotating them in a water-

bath maintained at $25.00 \pm 0.02^\circ$. Equilibrium was ascertained by repeated analysis after varying periods of time, and by approach from supersaturation. Alcohol-rich mixtures reached equilibrium more slowly than those which were water-rich. The yellow color of the chromate was visible even in absolute alcohol.

Analyses were made by evaporating weighed samples of the saturated solutions to dryness, and were reproducible to about ± 3 in the last reported digit. Densities were determined with calibrated pipets and with a pycnometer, and are estimated correct to one part per thousand.

Saturated soln.			Saturated soln.		
Solvent	Wt. %	Density	Solvent	Wt. %	Density
Vol. %	K_2CrO_4		Vol. %	K_2CrO_4	
C_2H_5OH			C_2H_5OH		
0	39.67	1.387	60.0	1.238	0.905
10.00	30.69	1.263	75.0	0.160	.863
20.00	21.70	1.152	85.0	.035	.834
30.00	13.50	1.062	95.0	.021	.801
40.00	7.19	0.992	100	.005	.786
50.00	3.214	.942			

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Two Liquid Phases in the Lithium-Ethylamine System at 0° ¹

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Lithium has been reported to be "extremely soluble" in ethylamine.² Investigation of this system at 0° has shown that at equilibrium there are two liquid phases present, similar to the behavior of sodium-ammonia solutions³ at low temperatures, where the system has a critical solution temperature in the neighborhood of -45° .

Eastman "anhydrous" ethylamine was dried by refluxing over lithium until the appearance of the deep blue color, which is observed with solutions of the alkali metals in ammonia and lower primary amines. This anhydrous ethylamine was distilled in a dry helium atmosphere into a glass tube (containing an excess of clean lithium) maintained at 0° with an ice-bath. Almost immediately the deep blue color appeared in the distillate which was vigorously agitated by means of a magnetic stirrer. After the resulting lithium-ethylamine system was equilibrated at 0° , it was observed that two liquid layers separated when the stirring was stopped. The upper layer was deep blue in color and somewhat smaller in volume than the colorless lower layer. Due to slight convection currents, streamers of the blue colored phase slowly circulated through the colorless and slightly denser phase.

In this study great care was observed to keep air and moisture out of the system. Unlubricated ground glass joints sealed with mercury were used throughout, and inert gas atmospheres were employed to eliminate contact of air with the purified ethylamine and lithium.

The apparatus used in this exploratory study was not adapted to the sampling of a two-phase system, so that no information was obtained on the composition of the two layers. Further work on this system has been set aside and therefore, the above observations are being reported at this time.

Seiler has stated⁴ that a trace of ammonia is

(1) The Knolls Atomic Power Laboratory is operated by the General Electric Company for the Atomic Energy Commission. The work reported here was carried out under contract No. W-31-109 Eng-52.

(2) G. N. Lewis and F. G. Keyes, *THIS JOURNAL*, **35**, 340 (1913).

(3) C. A. Kraus and W. W. Lucasse, *ibid.*, **44**, 1949 (1922).

(4) E. F. Seiler, *Astrophysical J.*, **52**, 129 (1920).

needed to catalyze the formation of a lithium-ethylamine solution and that the blue color appeared only after ten hours of stirring. No phase separation was observed in her work. The difference between these earlier observations and those reported here is considered to be entirely due to the relative cleanliness of the two systems with respect to air and moisture.

From this investigation the following preliminary conclusions can be drawn.

1. Ethylamine and lithium form two liquid phases at 0° , one blue, the other colorless.

2. The densities of the two phases are nearly equal, the colorless phase being the denser.

3. No catalyst is needed to initiate the solution of lithium in ethylamine, providing that the solvent is adequately dried and air is kept out of the system. With these precautions, the lithium dissolves rapidly.

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The Catalytic Hydrogenolysis of Proteins and Related Model Compounds¹

BY H. A. LILLEVIK² AND W. M. SANDSTROM

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Introduction

Adkins³ has shown that the carbon-to-nitrogen linkage in amides is cleaved at high temperatures and pressure by hydrogen in the presence of catalysts such as copper chromite or Raney nickel. Our purpose was to apply this reaction to proteins and to compare the results with those obtained upon some related model compounds. Zein and acetyl zein were examined together with nylon, polyacrylamide, butyl hippurate and acetamide. Since *n*-butyl alcohol employed as solvent could enter into the reaction, studies were included to differentiate the products of butanolysis from those due to hydrogenolysis. The products were examined to determine the extent of the two reactions upon the primary and secondary (peptide) amide linkages.

A survey of the literature reveals that no attempt has been made to apply Adkins' reduction to proteins, their derivatives or split products. Milder reducing agents such as cyanide or sodium-alcohol have been used; however, these are essentially without effect upon the peptide or amide linkages. Alcoholysis, particularly with methanol or ethanol under pressure, results in partial cleavage of proteins with loss of ammonia and volatile amines. Many of these reactions are considered in a survey article.⁴

(1) From part of a thesis submitted by Hans A. Lillevik to the Graduate School of the University of Minnesota in partial fulfillment of the requirements for the degree of Doctor of Philosophy. Published with the approval of the Director of the Minnesota Agricultural Experiment Station as Journal Series No. 2730.

(2) Kedzie Chemical Laboratory, Department of Chemistry, Michigan State College, East Lansing, Mich.

(3) H. Adkins, "Reactions of Hydrogen with Organic Compounds over Copper-Chromium Oxide and Nickel Catalysts," University of Wisconsin Press, Madison, Wisconsin, 1937, pp. 112-119.

(4) R. M. Herriot, "Advances in Protein Chemistry," Vol. III, The Academic Press, Inc., New York, N. Y., 1947, p. 169.