of tetralin are: f. p. −35.80°; b. p. (760 mm.) 207.57°; n^{20}_D 1.54135; d^{20}_4 0.9702.

Both naphthalene and tetralin were completely hydrogenated to decalin under all the conditions tried (Tables I and II). The liquid catalyzate gave no temperature rise when 2 cc. of it was shaken for three minutes in a test-tube with 2 cc. of nitrating mixture (1 vol. sulfuric acid d. 1.84 plus 2 vols. nitric acid d. 1.42), this qualitative test showing the absence of more than 3% of naphthalene or tetralin. The physical constants (n^{20}_D, d^{20}_4, δ (specific dispersion)[9]) of the catalyzates agreed with those of mixtures of *cis-* and *trans-*decalin.[10] The catalyzate composite boiled at 187.1–194.1° at 760 mm.

TABLE I

VAPOR PHASE HYDROGENATION OF NAPHTHALENE OVER NICKEL CATALYST

Hrs.	Pressure, mm.	Inlet H_2 l./hr./25°C.	Mole ratio $H_2/C_{10}H_8$	Catalyst temp., °C.	Liquid catalyzate g.	n^{20}_D	d^{20}_4	δ
15	755	1.4	26.0	123	3.7	1.4735	0.880	97
16	741	1.7	25.5	149	5.6	1.4729	.878	98
16	740	1.7	24.5	176	5.6	1.4732	.879	98
16	740	1.7	24.5	199	5.3	1.4719	.876	97

TABLE II

VAPOR PHASE HYDROGENATION OF TETRALIN OVER NICKEL CATALYST

Hrs.	Pressure, mm.	Inlet H_2 l./hr./25°C.	Mole ratio $H_2/C_{10}H_{12}$	Catalyst temp., °C.	Liquid catalyzate g.	n^{20}_D	d^{20}_4	δ
3	735	5.2	14.6	126	4.9	1.4740	0.881	98
3	735	5.1	14.6	151	5.4	1.4749	.883	98
3	735	4.8	14.6	175	4.7	1.4740	.881	98
3	735	5.2	14.6	200	5.1	1.4792	.892	98

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(9) $\delta = (nF - nC)/d \times 10^4$.

(10) Seyer and Walker (THIS JOURNAL, **60**, 2125 (1938)) reported d^{20}_4 0.8963 and 0.8699, b. p.° (760 mm.) 194.6 and 185.5 and n^{20}_D 1.48113 and 1.46968 for *cis-* and *trans-*decalins, respectively. The specific dispersion of decalin mixtures has been reported as about 98 (Ward and Fulweiler, *Ind. Eng. Chem., Anal. Ed.*, **6**, 396 (1934); Fuchs and Anderson, *Ind. Eng. Chem.*, **29**, 319 (1937); Ward and Kurtz, *Ind. Eng. Chem., Anal. Ed.*, **10**, 559 (1938); Grosse and Wackher, *ibid.*, **11**, 614 (1939); Bloch and Thomas, THIS JOURNAL, **66**, 1589 (1944)).

KOPPERS MULTIPLE FELLOWSHIP ON TAR SYNTHETICS
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RECEIVED SEPTEMBER 2, 1944

The Reduction of Diphenylnitrosamine in the Presence of Raney Nickel Catalyst and Platinum Catalyst[1]

BY GERALD F. GRILLOT

Paal and Yao[2] published in 1930 the results that they had obtained in reducing diphenylnitrosamine with hydrogen at about one atmosphere pressure and at room temperature in the presence of palladium deposited on calcium carbonate and barium sulfate. They had expected to obtain *unsym*-diphenylhydrazine, but instead diphenylamine and nitrogen were formed almost quantitatively.

In the hope that *unsym*-diphenylhydrazine might nevertheless be obtained by the use of a suitable catalyst, the author carried out the reduction using as catalyst both Raney nickel[3] and Adams platinum oxide.[4]

Thus, using diphenylnitrosamine prepared according to the method of Fischer,[5] melting after recrystallization at 66.5° as given by Witt,[6] reduction with hydrogen in the presence of Raney nickel catalyst at 35 lb. pressure in alcoholic solution at room temperature was substantially complete in an hour, 89% of the theoretical quantity of hydrogen was absorbed and an 83% yield of crude diphenylamine, melting at 53°, was obtained. The odor of ammonia was quite evident in the reduced solution. The benzoyl derivative of the diphenylamine was prepared and it melted at 179° as compared with the recognized melting point of 180°.[7] The mother liquor from the crystallization of the diphenylamine, with the addition of a few drops of acetic acid, gave no precipitate with benzaldehyde, indicating the absence of any *unsym*-diphenylhydrazine.

Using a somewhat more dilute solution containing in addition 5% of acetic acid by volume, four hours was required for the completion of the reaction, 85% of the theoretical amount of hydrogen was absorbed. Treatment of the solution with sodium hydroxide yielded ammonia equivalent to a 92% reduction.

Similar results were obtained using Adams platinum oxide catalyst in a slightly more dilute alcoholic solution.

These results confirmed the findings of Paal and Yao above mentioned, except that under our conditions a substantially quantitative yield of ammonia rather than of nitrogen resulted from the reduction.

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(1) Original manuscript received June 21, 1944.

(2) Paal and Yao, *Ber.*, **63B**, 57 (1930).

(3) Adkins, "Reactions of Hydrogen, etc.," University of Wisconsin Press, Madison, Wis., 1937, p. 20.

(4) Gilman, "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1932, p. 452.

(5) Emil Fischer, *Ann.*, **190**, 174 (1878).

(6) Witt, *Ber.*, **8**, 856 (1875).

(7) Shriner and Fuson, "Identification of Organic Compounds," Sec. Ed., John Wiley and Sons, Inc., New York, N. Y., 1940, p. 196.

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RECEIVED NOVEMBER 3, 1944

Interaction between Sodium Triphosphate and Salts of Polyvalent Cations as Shown by *p*H Measurements

BY LEA FRANKENTHAL

In the course of an investigation on sodium triphosphate an instantaneous acid shift was detected in solutions of this compound to which Mg^{++}, Ca^{++}, Mn^{++} or Al^{+++} salts were added. A similar qualitative observation of the decrease in *p*H has been made by H. Rudy[1] in a study of the dissolving effect of sodium triphosphate on calcium soaps. Accepted concepts concerning the

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(1) H. Rudy, *Angew. Chem.*, **54**, 447 (1941).

structure of sodium triphosphate suggest no ready explanation for this phenomenon.

Triphosphoric acid, $H_5P_3O_{10}$, a condensation of three molecules of orthophosphoric acid, is an inorganic analog of adenosine triphosphate according to Lohmann's formula. It was first made easily accessible by the preparative method of Huber.[2] The sodium salt, which is alkaline in reaction, has been used by C. Neuberg and coworkers[3] and others as a substrate for phosphatase. Because of the importance of the observed *p*H lowering in the study of the effect of salts on phosphatase activity a more precise, systematic series of experiments on the reaction of sodium triphosphate with salts of polyvalent cations was deemed desirable. The present communication reports the results of experiments on the *p*H reaction of mixtures of sodium triphosphate and magnesium chloride as a function of concentration.

Experimental Part

The sodium triphosphate used in the present experiments was obtained from Prof. C. Neuberg, who has previously published its characteristics and reactions,[3b] and to whom I should like to express my indebtedness for this kindness. The material was recrystallized and used as the hexahydrate ($Na_5P_3O_{10}\cdot 6H_2O$). When tested for free orthophosphoric acid with the Fiske and Subbarow reagent,[4] it showed only traces of orthophosphate. Also tests on mixtures with magnesium chloride in solution, even after boiling and cooling again, showed no greater orthophosphate than in the original reagent.

For preparation of the mixtures used in the present experiments, 0.2-ml. portions of a fresh 0.277 *M* solution of the sodium triphosphate were measured into each of a series of test-tubes containing water in suitable amounts. Graded volumes of 2.5 *M* magnesium chloride solution, ranging from 0.01 to 3.8 ml., were then added, the final volume in all cases being 4 ml. A saturated solution of magnesium chloride added to the sodium triphosphate in the same way produced a precipitate which did not dissolve entirely by shaking, so that it could not be included in the series. The order of addition of reagents is significant since addition of magnesium chloride to the undiluted triphosphate solution caused the deposition of a precipitate which was in some concentrations difficult to dissolve on subsequent dilution. The precipitate dissolved, however, on further addition of magnesium chloride.

The hydrogen ion concentrations of the various mixtures were determined potentiometrically with a bubbling hydrogen electrode, with which equilibrium was rapidly reached and reproducible results obtained. Measurements were started after three to five minutes of bubbling and continued until successive readings at one-minute intervals agreed within one millivolt. The electrode was checked daily against a standard acetate buffer.

The control magnesium chloride solutions, however, did not yield a constant potential with this electrode and accordingly their *p*H values were estimated colorimetrically with methyl red. This should be a valid procedure since the mixtures with triphosphate gave the same results by colorimetric and potentiometric measurement.

The distilled water used for dilution had a *p*H of about 6.3.

Results and Discussion.—The *p*H values obtained are plotted against the magnesium chloride concentration in Fig. 1. As may be seen, addition of magnesium chloride to a sodium triphosphate solution causes a depression of *p*H which is dependent on the concentration of magnesium chloride added. Mixtures with a high magnesium chloride content have lower *p*H values even than magnesium chloride alone at the same concentration. The curve for magnesium chloride alone shows only a gradual steady decrease in *p*H as the concentration is increased, whereas the mixtures with triphosphate show a sharp decrease to *p*H 6.8, a pronounced bending between *p*H 6.8 and 5.8 and a gently sloping straight line thereafter. A curve of the same shape but on a lower *p*H level was obtained in experiments carried out with triphosphate neutralized to litmus with hydrochloric acid.

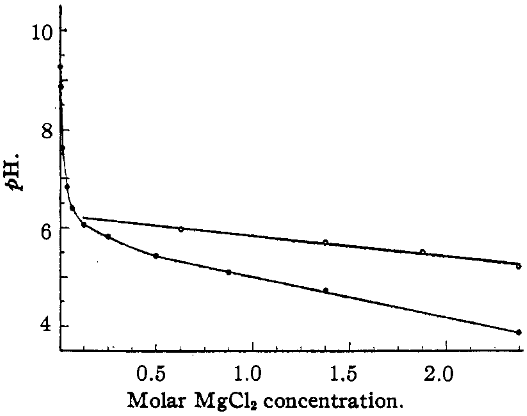

Fig. 1.—Variation of *p*H with the concentration of $MgCl_2$: Curve I, ○—○, $MgCl_2$ in H_2O; Curve II, ●—●, $MgCl_2$ in a 0.0139 molar solution of sodium triphosphate.

Variation in the *p*H from 6.8 to 5.8 involves variation in the molar triphosphate–magnesium chloride ratio from 0.5 to 0.05. It is significant that these same mixtures when heated to boiling form precipitates which dissolve again on cooling. This precipitation cannot be accounted for by hydrolysis of triphosphate and formation of $Mg_3(PO_4)_2$ for the latter would not redissolve on cooling. Nor would such an assumption correspond with the fact that mixtures of higher or lower magnesium chloride content fail to form precipitates when boiled.

In another series of experiments the concentration of magnesium chloride was kept constant at 2.2 ml. of 2.5 *M* $MgCl_2$ per 4 ml. total volume and the sodium triphosphate concentration was gradually increased from 0.04 to 1.6 ml. of 0.277 *M* solution. In this case the *p*H remained substantially constant at 4.66–4.68 throughout the tested range as against 5.4 for pure magnesium chloride solution of the same concentration.

These sets of experiments could not be carried out with Ca^{++} and Mn^{++} since above certain concentrations they form precipitates with sodium triphosphate. These dissolve in excess of the triphosphate in accordance with the observations of

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[2] H. Huber, *Angew. Chem.*, **50**, 323 (1937).

[3] (a) C. Neuberg, *Compt. rend. trav. lab. Carlsberg, serie chim.*, **22**, 366 (1938); (b) C. Neuberg and H. A. Fischer, *Enzymologia*, **2**, 241, 360 (1937–8).

[4] Fiske and Subbarow, *Science*, **70**, 381 (1929).

Rudy, Schloesser and Watzel.[5] Similar precipitates are also formed with Al^{+++} and sodium triphosphate, but only in a certain range of concentrations. In some ranges the precipitate dissolves on standing, while in others an excess of one of the reactants is necessary. The effect with Al^{+++} salts was demonstrated for the range where precipitation does not occur as follows: 0.2 ml. of a 0.139 *M* solution of sodium triphosphate was mixed with 1.5 ml. of 0.033 *M* aluminum chloride and diluted to a volume of 4 ml. The resulting solution had a *p*H lower than 3.1 when measured with brom thymol blue indicator, whereas aluminum chloride solution alone at the same concentration had a *p*H of 3.6.

Mixtures of triphosphate with potassium fluoride were tested as representative of the monovalent cation salts. Its addition had no effect on the *p*H of sodium triphosphate solution.

A possible explanation for this effect is that polyvalent cations can form complex compounds with sodium triphosphate, even though the ordinary formulation of such a reaction would not account for the extent of the acid shift. Since a depression in *p*H has also been observed in a solution of sodium glycerophosphate on addition of magnesium chloride, it is not unlikely that similar complexes also occur with phosphoric esters other than the sodium triphosphate. This possibility should be taken into consideration when the effect of salts upon phosphatase activity is investigated.

The author wishes to express her thanks to Dr. J. Leibowitz for his kind advice and interest in this work.

(5) H. Rudy, H. Schloesser and R. Watzel, *Chem. Abs.*, **35**, 1337 (1941).

CHEMICAL DEPARTMENT
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JERUSALEM, PALESTINE RECEIVED MAY 6, 1943

The Condensation of α-Picoline Methiodide with Aromatic Aldehydes

BY C. F. KOELSCH

Many aromatic aldehydes have been condensed with α-picoline to form stilbazole derivatives. The conditions used for bringing about this reaction are drastic, usually a mixture of the reagents with zinc chloride is heated at 180–230°. The procedure of Shaw and Wagstaff[1] involves somewhat milder conditions, boiling with acetic anhydride for ten hours, but even this procedure might not be applicable to aldehydes containing acid-sensitive groups.

It has been shown[2] that whereas α-picoline will not react with *p*-nitrosodimethylaniline, α-picoline methiodide will do so readily. But only a few condensations of α-picoline methiodide with aromatic aldehydes have been recorded: with *p*-dimethylaminobenzaldehyde,[3] and with *m*-dimethyl-, diethyl- and dipropylbenzaldehyde.[4] It has now been found that such condensations generally can be brought about under very mild conditions. When a solution of equivalent amounts of an aromatic aldehyde and α-picoline methiodide in a small amount of alcohol is treated with a few drops of piperidine and then allowed to stand at room temperature for some time, it deposits the condensation product in a crystalline form.

3′-Nitro-α-stilbazole methiodide forms coarse yellow needles from water that sinter at 235° and melt with decomposition at 256°[5]; yield 88% after eight hours.

Anal. Calcd. for $C_{14}H_{13}IN_2O_2$: C, 45.7; H, 3.5. Found: C, 45.8; H, 3.7.

4′-Hydroxy-α-stilbazole methiodide forms bright yellow prisms from water, that fall to a yellow powder on drying at 100° and then melt at 268–270°; yield 33% after three weeks.

Anal. Calcd. for $C_{14}H_{14}INO$: C, 49.6; H, 4.1. Found: C, 49.4; H, 4.3.

4′-Methoxy-α-stilbazole methiodide forms yellow needles from water that fall to a powder on drying and then melt with decomposition at 235–240°; yield 50% after eight hours.

Anal. Calcd. for $C_{15}H_{16}INO$: C, 50.9; H, 4.5. Found: C, 50.9; H, 4.5.

Furfurylidene-α-picoline methiodide, yellow prisms from water, that fall to an orange-yellow powder on drying, darkens at 200° and melts to a red liquid at 204–206°; yield 67% after eight hours.

Anal. Calcd. for $C_{12}H_{12}INO$: C, 46.0; H, 3.8. Found: C, 46.3; H, 4.2.

When the methiodides so obtained are heated at about 250° under reduced pressure, they dissociate, and the resulting stilbazole distils. For example 4′-methoxy-α-stilbazole methodide yields 4′-methoxy-α-stilbazole, colorless plates from dilute alcohol, m. p. 76° (reported[6] 75°). And furfurylidene-α-picoline methiodide yields furfurylidene-α-picoline, tan needles from dilute alcohol, m. p. 65–66° (reported[7] 51–53°).

Anal. Calcd. for $C_{11}H_9NO$: C, 77.2; H, 5.3. Found: C, 77.2; H, 5.2.

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(1) Shaw and Wagstaff, *J. Chem. Soc.*, 77 (1933).

(2) Kaufmann and Vallette, *Ber.*, **45**, 1739 (1912); *cf.* Mills and Smith, *J. Chem. Soc.*, **121**, 2726 (1922).

(3) Mills and Pope, *ibid.*, **121**, 946 (1922); *cf.* Doja and Prasad, *J. Indian Chem. Soc.*, **19**, 125 (1942).

(4) Cocker and Turner, *J. Chem. Soc.*, 59 (1940).

(5) Temperatures are corrected.

(6) Bialon, *Ber.*, **35**, 2788 (1902).

(7) Merck, *ibid.*, **21**, 2709 (1888).

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Catalytic Hydrogenation of Cyanoacetic Ethyl Ester

BY KEVIN E. KAVANAGH AND F. F. NORD

While the Hofmann degradation of succinimide is the best method for obtaining β-alanine used in the synthesis of pantothenic acid, it is rather tedious. Weygand[1] applied hydrogenation to an aliphatic nitrile, *viz.*, cyanoacetic ethyl ester, for this synthesis. He utilized platinum oxide (10%

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(1) F. Weygand, *Ber.*, **74B**, 256 (1941).