Values given by Garner and Abernethy (Table II), with one exception, indicate a rather regular rate of decrease in the amount of heat given off with the introduction of each successive nitro group into the ring. In no one of the several series covered by the writer (Table I) was this found to be true, the entrance of the second nitro group in each case causing the liberation of less heat than the third. This is contrary to both theory and observed fact and is ascribable to variation in the errors in determining heats of combustion, small variations in the percentage of error causing much larger variations in derived values. This would indicate that the new determinations of heats of combustion reported in this paper are probably low to the extent of 0.7%.

Summary

1. The heats of combustion of twenty-one compounds have been determined, no values for fourteen of these having been previously published. From these, heats of formation and of nitration have been calculated.
2. Study of the values determined and calculated indicate that those determined have a probable error of -0.7%.

DOVER, NEW JERSEY

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF WASHINGTON UNIVERSITY]

THE EFFECT OF *P*H UPON THE PRECIPITATION OF ZINC AMMONIUM PHOSPHATE

BY T. R. BALL AND MEYER S. AGRUSS

RECEIVED JULY 24, 1929 PUBLISHED JANUARY 8, 1930

The well-known method of determining zinc as zinc ammonium phosphate was first introduced by Tamm.[1] It has been studied by several investigators[2] with the final result that the precipitation is carried out in neutral or faintly acid solution, using diammonium phosphate as the precipitant. From five to twenty grams of ammonium chloride is present in the solution and the amount of precipitant may vary from ten to twenty times that of the weight of zinc estimated to be present. The precipitate formed at first is assumed by Olsen[3] to be amorphous $Zn_3(PO_4)_2$, which in the presence of ammonium salts is changed into crystalline Zn-

---

[1] Tamm, *Chem. News*, **24**, 148 (1871).

[2] Lösekann and Meyer, *Chem.-Ztg.*, **10**, 729 (1886); M. Austin, *Am. J. Sci.*, **8**, 206, 1899; *Z. anorg. Chem.*, **22**, 212 (1900); Langmuir, *Chem. News*, **79**, 183 (1899); Dakin, *Z. anal. Chem.*, **39**, 273 (1900); Voigt, *Z. angew. Chem.*, **22**, 2282 (1909); Langley, THIS JOURNAL, **31**, 1051 (1909); Finlay and Cumming, *J. Chem. Soc.*, **103**, 1004 (1913); see also Dede, *Ber.*, **61**, 2463 (1928).

[3] Olsen, "Quantitative Chemical Analysis," D. Van Nostrand Co., New York, **1904**, p. 82.

NH_4PO_4 by hot digestion. Practice varies as to the method of washing the precipitate, some authors using a 1% solution of diammonium phosphate followed by a mixture of water and alcohol. Langley[2] finds that washing with cold water gives satisfactory results.

While the accepted procedure calls for precipitation in a neutral or faintly acid solution, none of the previous investigators has determined the optimum *P*H. Fales[4] states that "the exact value of *P*H for which zinc ammonium phosphate is least soluble has not been definitely ascertained, but apparently is around a value of *P*H = 7.5." The present work has to do with the determination of the optimum *P*H.

Materials and Procedure

A high grade of zinc sulfate was mixed with C. P. ammonium sulfate mole for mole, dissolved in boiling water and twice recrystallized from hot water. The crystals were air-dried and analyzed by gentle ignition to $ZnSO_4$ in a large platinum crucible. The percentage of $ZnSO_4$ was found to be 40.19, 40.15 and 40.18% in three determinations; average, 40.173%; calcd. for $ZnSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$ = 40.193%. A standard was made by dissolving the salt in a weighed amount of water and all samples were taken by weighing the solution. In general, 5 g. of ammonium chloride and 10 cc. of 2 *N* sodium acetate were added to each zinc solution, followed by dilution to 140 cc. The solutions were then placed on a water-bath and when hot 10 cc. of 10% diammonium phosphate was slowly added from a pipet. The diammonium phosphate used conformed to the specifications of the Committee on Analytical Reagents of the American Chemical Society.[5] A solution of 1 g. in 10 cc. of water was colored pink by the addition of 2 drops of phenolphthalein solution. After two hours on the water-bath in a covered beaker, the precipitates were filtered onto Gooch crucibles, washed with about 150 cc. of cold water, 5 cc. of 95% alcohol and dried in the oven for one hour at 105°. The amount of zinc was then calculated on the assumption that the precipitate was $ZnNH_4PO_4$. In some cases larger amounts of ammonium chloride were added, as shown in the notes to Table I.

Where low *P*H values were desired, varying amounts of 1.0 *N* HCl were added just before the addition of the precipitant. To produce high *P*H values, 1.0 *N* NaOH or 10% NH_3 was added. All of these reagents were carefully tested and found to yield no precipitate with phosphate under the range of conditions used.

The *P*H values of the undiluted filtrates were determined with a hydrogen electrode against a normal calomel. This was the method followed for all the results shown in Table I which were obtained by Ball. Mr. Agruss followed much the same procedure except that he used an equivalent amount of ammonium acetate in place of sodium acetate and determined the *P*H by the Gillespie drop ratio method, using the Clark and Lubs indicators. The results of Mr. Agruss, forty-seven in number, are not given in the table since they are so consistent with those of the senior author that their inclusion would add nothing to the interpretation. They simply show that the presence of sodium salts, in the concentrations used,

---

[4] Fales, "Inorganic Quantitative Analysis," The Century Co., New York, 1925, p. 257.

[5] *Ind. Eng. Chem.*, 19, 645 (1927).

are without effect. The object of adding the sodium acetate was to increase the buffer action.

Experimental

The results are given in Table I, which is self-explanatory. Unless otherwise stated each solution contained 5 g. of ammonium chloride. The average error for each *P*H value is plotted against the *P*H in Fig. 1.

TABLE I

EFFECT OF *P*H ON THE PRECIPITATION OF ZINC AMMONIUM PHOSPHATE

5 g. of NH_4Cl; 1 g. of $(NH_4)_2HPO_4$; 10 cc. of 2 *N* $NaC_2H_3O_2$; final volume, 150 cc.

No.	Zn taken, g.	Zn found, g.	Error, mg.	*P*H	No.	Zn taken, g.	Zn found, g.	Error, mg.	*P*H
1	0.0881	0.0798	−8.3	4.2[a]	19	0.0726	0.0726	0.0	6.6[c]
2	.0883	.0855	−2.8	4.7[a]	20	.0363	.0363	.0	6.7
3	.0877	.0874	−0.3	5.1[a]	21	.0263	.0266	+ .3	6.7
4	.0882	.0878	− .4	5.2[a]	22	.0717	.0716	− .1	6.7
5	.0880	.0876	− .4	5.4[a]	23	.0900	.0900	.0	6.9
6	.0877	.0876	− .1	5.4[a]	24	.0817	.0818	+ .1	6.9
7	.0887	.0883	− .4	6.2[a]	25	.0834	.0834	.0	7.1[d]
8	.0882	.0879	− .3	6.2[a]	26	.0851	.0852	+ .1	7.1[d]
9	.0888	.0888	.0	6.4[b]	27	.0888	.0891	+ .3	7.1[d]
10	.0885	.0887	+ .2	6.4[b]	28	.0892	.0894	+ .2	7.3[d]
11	.0884	.0882	− .2	6.4[b]	29	.0885	.0887	+ .2	7.4[e]
12	.0889	.0890	+ .1	6.4[b]	30	.0882	.0884	+ .2	7.6[d]
13	.0897	.0897	.0	6.4	31	.0892	.0896	+ .4	7.6[d]
14	.0898	.0899	+ .1	6.4	32	.0876	.0878	+ .2	7.7[d]
15	.0887	.0884	− .3	6.4	33	.0883	.0863	−2.0	7.8[e]
16	.0447	.0447	.0	6.5	34	.0887	.0844	−4.3	7.9[e]
17	.0183	.0181	− .2	6.5	35	.0884	.0793	−9.1	8.3[e]
18	.0548	.0548	.0	6.6					

[a] HCl added. [b] 10 g. of NH_4Cl. [c] 8 g. of NH_4Cl. [d] NaOH added. [e] 10% NH_3 added.

Discussion

Determinations 1 to 8 of Table I show that all results are low up to a *P*H of 6.2 and fall off very rapidly below 5.1. From a *P*H of 6.4 to 6.9 (Nos. 9 to 24) seven results show a zero error, five show slightly high results and four are low. The mean deviation from the theoretical over this range is zero. From a *P*H of 7.1 to 7.7 all results are high, with the exception of No. 25, but the error is not large. It should be noted, however, that whenever the *P*H exceeds 7.0, the precipitates are removed from the beaker with great difficulty and do not have the definite crystalline structure characteristic of those precipitated from the more acid solutions. Above a *P*H of 7.7 the zinc error is negative and very large. This is obviously due to the formation of a complex ion of zinc with free ammonia. Even at *P*H values as low as 6.6 the odor of ammonia is distinct from the hot solution.

A study of Fig. 1 shows that the curve crosses the zero axis at 6.6. This obviously is the optimum *P*H at which to make the determination. The results of Mr. Agruss, using ammonium acetate in place of the sodium salt, when similarly plotted, lead to the same conclusion.

The filtrates of Expts. 9 to 15, Table I, all showed a *P*H of 6.4 regardless of the fact that Nos. 9 to 12 contained twice as much ammonium chloride as the others. The range of 6.4 to 6.9 in *P*H shown in Nos. 13 to 24, which were all run with identical reagents, is doubtless due to variations in air circulation resulting in unequal volatilization of ammonia during the heating. However, all fall within a safe *P*H range, so that the conclusion seems justified that the two-hour heating period in a covered beaker automatically adjusts the acidity to the proper range. This was further investigated by preparing a solution containing 5 g. of NH_4Cl, 10 cc. of 2 *N* NaAc and 10 cc. of 10% $(NH_4)_2HPO_4$ in a total volume of 150 cc. The *P*H of this solution was 7.5 but it dropped to 6.9 after two hours of heating on the bath. Ten minutes of vigorous boiling, followed by dilution to the original volume with water, reduced the *P*H to 5.6. Obviously the solution should not be boiled.

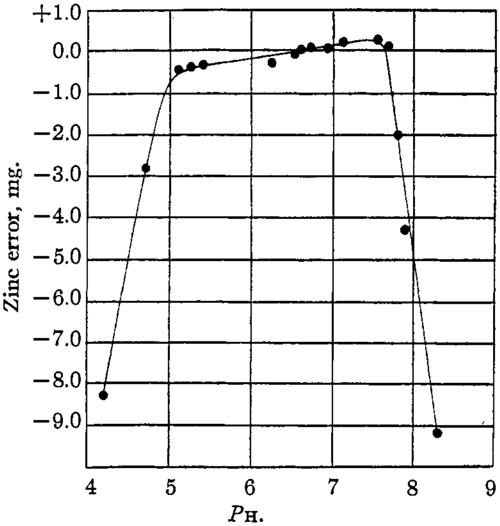

Fig. 1.—The effect of *P*H upon the precipitation of zinc ammonium phosphate.

Justification for the addition of sodium acetate to improve the buffer action is shown by the fact that the original solution referred to above was changed from a *P*H of 7.5 to 6.5 by the addition of 5 cc. of 1.0 *N* HCl. When the sodium acetate was left out the *P*H changed to 6.3, which is dangerously low (see Nos. 7 and 8 of Table I).

Summary

1. Satisfactory results may be obtained for the determination of zinc as zinc ammonium phosphate over a *P*H range of 6.4 to 6.9.
2. The optimum *P*H is 6.6.
3. The concentration of ammonium chloride between five and ten grams per 150 cc. is without appreciable effect.
4. The precipitate is not crystalline at *P*H values above 7.0 and is removed from the beaker with difficulty.

5. Below a P_H of 5.1 and above 7.7 the results are much too low.

6. Solutions containing 5 to 10 g. of NH_4Cl, 10 cc. of 2 *N* $NaC_2H_3O_2$ and 10 cc. of 10% $(NH_4)_2HPO_4$ in 150 cc. have a P_H of 7.5 but automatically fall to a range of 6.4 to 6.9 on the water-bath when heated for two hours.

7. Washing of the precipitate with cold water seems to yield satisfactory results.

ST. LOUIS, MISSOURI

[CONTRIBUTION FROM GATES CHEMICAL LABORATORY, CALIFORNIA INSTITUTE OF TECHNOLOGY, NO. 228]

THE QUANTUM YIELD IN THE PHOTOCHEMICAL DECOMPOSITION OF HYDROGEN AZIDE

BY ARNOLD O. BECKMAN AND ROSCOE G. DICKINSON

RECEIVED JULY 27, 1929 PUBLISHED JANUARY 8, 1930

Introduction

In a previous paper[1] it has been shown that gaseous hydrogen azide, HN_3, is decomposed by ultraviolet radiation of wave length less than 2200 Å. The products of the reaction were found to be hydrogen, nitrogen and ammonia (ammonium azide); no hydrazine was found.

The decompositions of aqueous solutions of HN_3 by ultraviolet radiation has been studied by Gleu[2] who found that here the products were largely hydroxylamine and nitrogen with small amounts of ammonia and traces of hydrazine.

The present paper is concerned with the quantum yields in the decomposition of gaseous HN_3 produced by monochromatic radiation, and with the effect of pressure on these yields.

Apparatus and Procedure

A diagram of the apparatus is shown in Fig. 1. Anhydrous gaseous HN_3, prepared as before[1] from sulfuric acid and NaN_3, was stored in the 1-liter bulb, A, which was attached to a vacuum system. Attached to the same system were a quartz reaction vessel, N, in which the HN_3 was irradiated, a McLeod gage, and a quartz fiber gage, H. With the mercury cut-off, C, and the cock K closed and with the cut-off M open, a desired quantity of HN_3 was admitted to the system with the aid of the doser, B. The HN_3 was frozen out by applying liquid air at P and any traces of non-condensable gas were pumped off. The cut-off M was then closed and the liquid air removed from P allowing the HN_3 to vaporize into the reaction cell, N. The pressure of the HN_3 was read from the difference in the mercury levels in the two arms of M. In those cases where the pressure of HN_3 was too small to be measured satisfactorily in this manner, this procedure was slightly modified to permit the measurement of the HN_3 pressure on the McLeod gage. The reaction cell, N, was a quartz cylinder 2.5 cm. in diameter and

---

[1] Beckman and Dickinson, THIS JOURNAL, **50**, 1870 (1928).

[2] Karl Gleu, *Ber.*, **61**, 702 (1928).