The heat of solution, $H_3PO_4(l) + aq = H_3PO_4$ (84.40%), is −1983 cal./mole of H_3PO_4.[15] Thus, the heat of formation of H_3PO_4 (84.40%) is −305,553 cal./mole of H_3PO_4.

Each measurement of a heat of solution was made with 900 g. of 4 molal hydrochloric acid in the solution calorimeter. Electrical calibrations over the same temperature interval were made immediately before and after the measurement of the heat of solution. The after-period of the first calibration thus was the fore-period of the heat of solution, and the after-period of the heat of solution was the fore-period of the second calibration. A starting temperature was chosen that would put the temperature at the end of the dissolution within a few hundredths of a degree of 25°, and temperature corrections were unnecessary. The following heats of solution were obtained. $H_3PO_4 \cdot 1.0055H_2O(l)$, 3 to 7 g.: −1773, −1775, −1784, −1784, or an average of −1779 ± 5 cal./mole of H_3PO_4. $Ca(OH)_2$ (c), 1 to 2 g. in HCl solution to which had been added the stoichiometric amount of $H_3PO_4 \cdot 1.0055H_2O$: −31,462, −31,325, −31,314, −31,186, −31,316, or an average of −31,285 ± 100 cal./mole of $Ca(OH)_2$. $H_2O(l)$, 1 to 10 g.: −64.7, −66.4, −63.7, −64.2, −65.2, or an average of −64.9 ± 1.5 cal./mole of H_2O. In three of the runs, ten times the stoichiometric amount of water was used in an attempt to increase the accuracy of the measurement, but the results were the same as those of the other runs. $Ca(H_2PO_4)_2 \cdot H_2O(c)$, 5 to 9 g. in HCl solution to which had been added the stoichiometric amount of H_2O indicated by eq. 1: 3476, 3455, 3426, 3423, 3444, 3477, or an average of 3450 ± 22 cal./mole of $Ca(H_2PO_4)_2 \cdot H_2O$.

The results indicated that no correction was required for the effect of the size of the charge. In five tests, the energy of breaking the glass sample bulb was within the limits of error of the measurements.

Substitution of the molal heats of solution in eq. 1 leads to a value of −38,228 ± 103 cal. for the heat of reaction at 25°. Heats of formation at 25°, in cal./mole, are: $H_3PO_4 \cdot 1.0055H_2O(l)$, −305,553; $Ca(OH)_2(c)$,[16] −235,800; $H_2O(l)$, −68,317. The heat of formation of $Ca(H_2PO_4)_2 \cdot H_2O(c)$ at 25° then is −816,820 cal./mole.

The heat of the reaction

$$2(H_3PO_4 \cdot 1.0055H_2O)(l) + Ca(OH)_2(c) = Ca(H_2PO_4)_2(c) + 2H_2O(l) + aq \quad (2)$$

was determined similarly. The heat of solution of 4 to 9 g. of $Ca(H_2PO_4)_2(c)$ in 4 molal HCl containing the stoichiometric amount of water indicated by eq. 2 was −1104, −1012, −1024, −1104, −1052, −1054, or an average of −1059 ± 31 cal./mole. The heat of reaction (eq. 2) at 25° then is −35,770 cal., and the heat of formation at 25° of $Ca(H_2PO_4)_2$ (c) is −746,040 cal./mole. The heat of hydration

$$Ca(H_2PO_4)_2(c) + H_2O(l) = Ca(H_2PO_4)_2 \cdot H_2O(c) \quad (3)$$

then is −2460 cal./mole at 25°.

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[15] Unpublished TVA data.

[16] National Bureau of Standards Circular 500, U. S. Govt. Printing Office, Washington, D. C., 1952.

WILSON DAM, ALABAMA

[CONTRIBUTION FROM THE PYROTECHNICS CHEMICAL RESEARCH LABORATORY, PICATINNY ARSENAL]

The Reaction between Mercury and Nitrogen Dioxide

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The reaction between mercury and nitrogen dioxide has been investigated in the presence of nitric oxide and oxygen. The nitric oxide to oxygen ratios studied were: (A) greater than 2, (B) 2 to 1.33, (C) 1.33 to 1.00 and (D) less than 1.00. The reaction for (A) appears to be $4Hg + 6NO_2 = Hg_2(NO_3)_2 + Hg_2(NO_2)_2 + 2NO$. In the presence of excess oxygen, in (B), (C) and (D) the nitric oxide formed is reconverted into nitrogen dioxide. The total amount of nitric oxide which may react in this manner is expressed by the relationship $[NO] = [NO_i] + \sum_1^1 \frac{[NO_i]}{3n}$ where $[NO_i]$ is the initial quantity. For nitric oxide to oxygen ratios of 1.33 to 1.00 the net reaction is $4Hg + 4NO_2 + O_2 = Hg_2(NO_3)_2 + Hg_2(NO_2)_2$.

Introduction

In 1928, Pierce and Noyes[1] postulated that mercuric and/or mercurous nitrite were formed during the initial stages of the reaction between mercury and nitrogen dioxide, followed by the formation of nitric oxide and nitrogen. They did not, however, present experimental evidence to verify the hypothesis. In the course of a study of the kinetics of the decomposition of various inorganic nitrates, the reaction between mercury and nitrogen dioxide became of interest, since the gaseous decomposition products were collected by mercury displacement. The reaction also presented a potential method for the analysis of mixtures of nitrogen dioxide, nitric oxide and oxygen.

Experimental

The following reagents were used: mercury, pyrogallol, sodium sulfate, potassium hydroxide, sulfuric acid (Fisher Scientific Company), nitric acid, acetic acid (J. T. Baker Chemical Company), ferric ammonium sulfate, ferrous ammonium sulfate and potassium thiocyanate (Mallinckrodt Chemical Works). All the chemicals were of C.P. grade. The alkaline pyrogallol and mixed acids (nitric and sulfuric) were prepared as described by Johnson.[2] The gases, nitric oxide, oxygen and nitrogen dioxide, were purchased from the Matheson Company, Inc., and were 98.0, 99.6 and 98.0% pure, respectively. Gas sampling bulbs having a 100-ml. capacity were made of Pyrex glass with a three-way stop-

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[1] W. C. Pierce and W. A. Noyes, Jr., THIS JOURNAL, **50**, 2179 (1928).

[2] C. L. Johnson, *Anal. Chem.*, **24**, 1572 (1952).

cock at each end, and were supplied by H. A. Kummer and Company. A saturated solution of ferric ammonium sulfate in 5% nitric acid was used as the indicator. A Fisher Precision Gas Analyzer, Model No. 10-601-1, was employed for the gas absorption analyses.

Procedure.—Three test-tubes (50-ml. capacity each) containing 5 ml. of mercury were filled with nitrogen dioxide and closed by means of rubber stoppers. In addition, measured amounts of nitric oxide, oxygen and an excess of mercury (5 to 10 ml.) were placed in seven gas sampling bulbs. The bulbs and test-tubes were shaken, during which time the nitrogen dioxide reacted with the mercury. The reaction time varied from 2 to 5 minutes. If the samples were not agitated, the reaction time increased to periods greater than 24 hours, due to a protective film of products coating the mercury. It was assumed that the reaction was completed when the characteristic brown color of nitrogen dioxide no longer could be observed.

The solid reaction products were dissolved in 5% nitric acid and tested for the mercurous ion by the addition of dilute hydrochloric acid. The solution was then filtered and tested for the presence of the mercuric ion by means of the diphenyl carbazide test.[3] The brown ring test using ferrous ammonium sulfate, acetic and sulfuric acids, served to distinguish between and identify the presence of the nitrate and/or the nitrite ions. X-Ray powder diagrams were also obtained for the reaction products.

The gases were analyzed by standard gas absorption methods.[2] In removing the mercury from the gas bulb, care was taken not to withdraw it completely in order to avoid losses of the mercurous salts, which remain on the upper surface of the liquid metal. By means of a small suction bulb, 25 ml. of a 5% solution of nitric acid was drawn into the gas sampling bulb to dissolve the solid reaction products. The resulting solution was transferred to a 400-ml. beaker. This procedure was carried out three times, the total volume being no more than approximately 100 ml. The solution was then filtered into a 400-ml. beaker in order to remove the excess mercury. Fifty milliliters of concentrated nitric acid was added to the supernatant liquid and the solution was heated on a hot plate to just below boiling, oxidizing the mercurous ion to the divalent state. During the reaction the solution turned yellowish in color as a result of the formation of nitrogen dioxide. The disappearance of this coloration indicated completion of the reaction. After the solution cooled, 100 ml. of water and two or three drops of ferric alum indicator were added which was then followed by a titration with 0.10000 *N* potassium thiocyanate.

Results

1. The nitrate, nitrite and mercurous ions and nitric oxide were identified in the solid and gaseous products, respectively. The X-ray powder diagrams could not be used to identify these products since only the pattern for hydrated mercurous nitrate is reported. The *d*-spacings do not correspond to any other known mercury compounds including the oxides. These results indicate that the reaction may be described by the general equation

$$a\text{Hg} + b\text{NO} + c\text{O}_2 = d\text{Hg}_2(\text{NO}_3)_2 + e\text{Hg}_2(\text{NO}_2)_2 + f\text{NO}' \quad (1)$$

Nitric oxide and oxygen react to form nitrogen dioxide. NO′ is the nitric oxide produced by reaction (1).

2. The stoichiometry of the reaction was determined from the mercury, nitrogen and oxygen balances between the reactants and products.

"Hg" balance: $[\text{Hg}] = 2[\text{Hg}_2(\text{NO}_3)_2] + 2[\text{Hg}_2(\text{NO}_2)_2] \quad (2)$

The brackets refer to molar quantities.

"N" balance:

$$[\text{NO}] = 2[\text{Hg}_2(\text{NO}_3)_2] + 2[\text{Hg}_2(\text{NO}_2)_2] + [\text{NO}'] \quad (3)$$

"O" balance:

$$[\text{NO}] + 2[\text{O}_2] = 6[\text{Hg}_2(\text{NO}_3)_2] + 4[\text{Hg}_2(\text{NO}_2)_2] + [\text{NO}'] \quad (4)$$

Substitution for [NO] equation 3, in equation 4 gives

$$[\text{O}]_2 = 2[\text{Hg}_2(\text{NO}_3)_2] + [\text{Hg}_2(\text{NO}_2)_2] \quad (5)$$

Substitution for $[\text{Hg}_2(\text{NO}_2)_2]$ equation 2, in equation 5

$$[\text{O}_2] = [\text{Hg}_2(\text{NO}_3)_2] + \frac{[\text{Hg}]}{2} \quad (6)$$

$$[\text{Hg}_2(\text{NO}_3)_2] = [\text{O}_2] - \frac{[\text{Hg}]}{2} \quad (7)$$

By solving for $[\text{Hg}_2(\text{NO}_2)_2]$ in equation 5, equation 8 is obtained

$$[\text{Hg}_2(\text{NO}_2)_2] = [\text{O}_2] - 2[\text{Hg}_2(\text{NO}_3)_2] \quad (8)$$

Substitution for $[\text{Hg}_2(\text{NO}_3)_2]$ equation 7, in equation 8 gives

$$[\text{Hg}_2(\text{NO}_2)_2] = [\text{Hg}] - [\text{O}_2] \quad (9)$$

3. In order to establish the stoichiometry of the reaction, the ratios of the coefficients in equation 1 (*d*/*e*, *b*/*a*, *a*/*c*, 2*c*/*f*) were calculated from the relationships: *d*/*e*, equation 7 divided by equation 9

$$\frac{d}{e} = \frac{[\text{Hg}_2(\text{NO}_3)_2]}{[\text{Hg}_2(\text{NO}_2)_2]} = \frac{2[\text{O}_2] - [\text{Hg}]}{2([\text{Hg}] - [\text{O}_2])} \quad (10)$$

b/*a*, equation 3 divided by equation 2

$$\frac{b}{a} = \frac{[\text{NO}]}{[\text{Hg}]} = \frac{2([\text{Hg}_2(\text{NO}_3)_2] + [\text{Hg}(\text{NO}_2)_2]) + [\text{NO}']}{2([\text{Hg}_2(\text{NO}_3)_2] + [\text{Hg}_2(\text{NO}_2)_2])} \quad (11)$$

a/*c*, equation 2 divided by equation 5

$$\frac{a}{c} = \frac{[\text{Hg}]}{[\text{O}_2]} = \frac{2([\text{Hg}_2(\text{NO}_3)_2] + [\text{Hg}_2(\text{NO}_2)_2])}{2[\text{Hg}_2(\text{NO}_3)_2] + [\text{Hg}_2(\text{NO}_2)_2]} \quad (12)$$

$$\frac{2c}{f} = \frac{2[\text{O}_2]}{[\text{NO}']} = \frac{[\text{NO}_2]}{[\text{NO}']} \quad (13)$$

4. The ratios *d*/*e*, *b*/*a*, *a*/*c* and 2*c*/*f* were determined from the experimental data in Table I, and are given in Table II. It should be noted that the sum of the amounts of mercurous nitrate and mercurous nitrite is equal to total mercurous ion.

TABLE I

REACTIONS OF KNOWN MIXTURES OF NITRIC OXIDE AND OXYGEN

1 Sample no.	2 Gas	3 Before reaction amount, mmoles	4 After reaction amount, mmoles	5 Amount of Hg_2^{++} mmoles	6 Total gas found,[d] mmoles
1[a]	NO	1.740	0.23	0.825	1.87
	O_2	1.264	.00		1.24
2[a]	NO	1.123	.15	.558	1.27
	O_2	0.872	.00		0.84
3[a]	NO	0.640	.00	.369	0.74
	O_2	1.662	1.03		1.58
4[b]	NO	2.450	1.39	.496	2.38
	O_2	0.774	0.00		0.74
5[c]	NO	2.780	1.86	.409	2.68
	O_2	0.651	0.00		0.61
6[b]	NO	0.717	0.00	.378	0.755
	O_2	2.375	1.638		2.205, 2.351[e]

[a] Temperature 28.5°, pressure 742.7 mm. [b] Temperature 23.0°, pressure 747.5 mm. [c] Temperature 24.0°, pressure 741.6 mm. [d] Based on the formation of equimolecular mixture of the mercurous nitrate and nitrite. [e] Calculated from equation 20.

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(3) F. Feigl, "Spot Tests," Elsevier Publishing Co., Inc., New York, N. Y., 1946, p. 304.

TABLE II

A. EXPERIMENTAL RATIOS OF REACTANTS AND PRODUCTS

Sample no.	$\frac{[NO]}{[O_2]}$	$\frac{[Hg_2(NO_3)_2]}{[Hg_2(NO_2)_2]}$ d/e	$\frac{[NO]}{[Hg]}$ b/a	$\frac{[Hg]}{[O_2]}$ a/c	$\frac{[NO_2]}{[NO']}$ $2c/f$
1	3.17	1.29	1.49	1.28	3.16
2	4.27	1.46	1.47	1.26	3.42
3	1.38	1.14	1.14	1.30	7.57
4	1.29	1.30	1.18	1.28	7.50
5	0.39	2.65	1.00	1.16	∞
6	0.30	20.0	1.00	1.03	∞

B. THEORETICAL RATIOS OF REACTANT AND PRODUCTS

Sample no.	$\frac{[NO]}{[O_2]}$	$\frac{[Hg_2(NO_3)_2]}{[Hg_2(NO_2)_2]}$ d/e	$\frac{[NO]}{[Hg]}$ b/a	$\frac{[Hg]}{[O_2]}$ a/c	$\frac{[NO_2]}{[NO']}$ $2c/f$
1[a]	2.00	1	1.5	1.33	3.00
2[b]	1.33	1	1	1.33	∞
3[c]	1.00	∞	1	1	∞

[a] $4Hg + 6NO + 3O_2 = Hg_2(NO_3)_2 + Hg_2(NO_2)_2 + 2NO'$. [b] $4Hg + 4NO + 3O_2 = Hg_2(NO_3)_2 + Hg_2(NO_2)_2$. [c] $2Hg + 2NO + 2O_2 = Hg_2(NO_3)_2$.

5. The numbers of millimoles of nitric oxide formed during the reaction were: 0.23, 0.15, 1.39 and 1.86 for samples 1, 2, 4 and 5, respectively, and 0.00 for samples 3 and 6. The numbers of millimoles of residual oxygen were: 1.03 and 1.64 in samples 3 and 6, respectively, and 0.00 for samples 1, 2, 4 and 5.

Discussion

For the systems which had a nitric oxide to oxygen ratio greater than 2, samples 1 and 2, the average values for d/e, b/a, a/c, and $2c/f$, were found to be 1.38, 1.48, 1.28 and 3.29, respectively; see Table II. A close approach to these ratios is given by equation 14 with corresponding stoichiometric ratios of 1, 1.5, 1.33 and 3, respectively.

$$4Hg + 6NO + 3O_2 = Hg_2(NO_3)_2 + Hg_2(NO_2)_2 + 2NO' \quad (14)$$

$$6NO + 3O_2 = 6NO_2 \quad (15)$$

Since it is the nitrogen dioxide which reacts with mercury, the final equation is

$$4Hg + 6NO_2 = Hg_2(NO_3)_2 + Hg_2(NO_2)_2 + 2NO' \quad (16)$$

It is apparent from equation 16 that, in the presence of excess oxygen, where $[NO]/[O_2]$ is approximately equal to or greater than 1.33 (see equation 18) but less than 2 (equation 14), additional nitrogen dioxide is formed from NO which further reacts with mercury. This accounts for the increased $2c/f$, $[NO_2]/[NO']$ ratios of 7.57 and 7.50 for samples 3 and 4, respectively, Table II.

The total amount of nitric oxide which may react in the above cyclic manner is related to the initial amount of nitric oxide in the system by the following expression derived from equation 16

$$[NO] = [NO_i] + \sum_{1}^{n} \frac{[NO_i]}{3n} \quad (17)$$

where n is the number of cycles and $[NO_i]$ is the initial amount of nitric oxide placed in the system. The theoretical amounts of nitric oxide (millimoles) which may be formed were calculated to be: 0.09, 1.06 and 1.43 in samples 1, 4 and 5, respectively; and zero in samples 2, 3 and 6. The corresponding observed values are 0.23, 1.39 and 1.86; 0.15 for sample 2 and 0.00 for samples 3 and 6. The theoretical values for residual oxygen (millimoles) are 1.18 and 1.84 for samples 3 and 6; and zero in samples 1, 2, 4 and 5. The corresponding experimental values are: 1.03 and 1.64 for samples 3 and 6, and 0.00 for samples 1, 2, 4 and 5. Since the principal reaction represents 85 to 97% of the total reaction, as indicated by a 3 to 15% difference between the theoretical and observed results for the nitric oxide balance, the calculated and observed results are considered to be in relatively good agreement; see Table I. This may be taken as additional evidence for confirming equation 16.

When the ratio of nitric oxide to oxygen is significantly less than 1.33 as in samples 5 and 6, equation 16, theoretically, reduces to

$$4Hg + 4NO + 3O_2 = Hg_2(NO_3)_2 + Hg_2(NO_2)_2 \quad (18)$$

$$\text{where: } 4NO + 3O_2 = 4NO_2 + O_2 \quad (19)$$

In this case the ratio of mercurous nitrate to mercurous nitrite, d/e, increases significantly above the theoretical value of unity. The values are 2.65 for sample 5 and 20.0 for sample 6. The ratio of mercury to oxygen, a/c, is significantly less than that of the other samples which have an average value of 1.28, compared with 1.16 and 1.03 for samples 5 and 6, respectively. This indicates that when the amount of oxygen is greater than that required to convert the total amount of nitric oxide to an equimolecular mixture of mercurous nitrite and nitrate, the excess oxygen oxidizes some of the mercurous nitrite to the nitrate. In the case of sample 6, the ratios of d/e, a/c and $2c/f$ indicate that almost all of the nitrite had been oxidized to the nitrate and the net reaction is

$$2Hg + 2NO_2 + O_2 = Hg_2(NO_3)_2 \quad (20)$$

$$\text{where: } 2NO + 2O_2 = 2NO_2 + O_2$$

This equation accounts for 99% of the oxygen in the system. Sample 5, which contained proportionately less oxygen than sample 6, undergoes an amount of reaction intermediate between that represented by equations 20 and 18, indicated by the ratios presented in Table II.

The over-all results show that the nitric oxide to oxygen ratio determines the stoichiometry of the reaction. For values of 2 and greater, the reaction is represented by equation 16; for values of 1.33 or less, equation 18 or 20 may represent the stoichiometry. Between the values of 2 and 1.33 the reaction is represented by an equation which is intermediate to equations 16 and 18. The exact stoichiometry depends upon the relative closeness of the nitric oxide to oxygen ratio to the value of 2 or 1.33. If the initial amounts of nitric oxide and oxygen in the system are known, then the reaction may be predicted from equation 17.

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