pressibility data at 100 atmospheres, the temperature drop in expanding through the calorimeter would be slightly less than 0.04°. When the total temperature rise is 6°, this factor causes the final result to be too high by about 0.6%. This correction is less as the pressure is increased because $-(dT/dp)H$ approaches zero and finally changes sign.

Faulty technic in operating the apparatus is probably the main cause for errors in the final result. An average experiment takes about four hours and all conditions should be very constant for at least half an hour before the readings are taken. This is rather difficult to do since quite frequent gas compression is necessary with the high rates used.

During a satisfactory experiment the temperature of the calorimeter does not change more than 0.01° in half an hour. A correction can be applied for a slight temperature change by taking into account the water equivalent of the calorimeter and the rate of temperature change. The water equivalent is roughly one kilogram. A 0.01° rise indicates that 10 calories have been absorbed and if the rise takes place in 30 minutes, 0.3 calorie is being absorbed per minute. This correction is usually less than 0.5%. The results are reproducible to something better than 0.5% under good conditions.

Summary

A constant temperature continuous flow adiabatic calorimeter has been described. The apparatus for measurement of the specific heats of gases at ordinary temperatures and up to 1000 atmospheres pressure is described. Typical results for nitrogen at 200 atmospheres are given together with the method of calculation.

URBANA, ILLINOIS

[CONTRIBUTION FROM THE PICATINNY ARSENAL]

THE HEATS OF COMBUSTION AND FORMATION OF AROMATIC NITRO COMPOUNDS

BY WM. H. RINKENBACH[1]

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Although numerous investigators have studied the relationship existing between the constitution and thermochemical constants of organic compounds and particular attention has been paid to this relationship as regards nitro explosives, stereoisomers, homologs, etc., there still exist gaps in the values available for series of compounds and their derivatives. As the availability of such physico-chemical constants is of increasing importance and certain data of this nature were desired for use in connection with other work, it was considered desirable to make accurate determinations of the heats of combustion of a number of aromatic nitro com-

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pounds and to calculate their heats of formation. For purposes of comparison and confirmation, it was decided to make similar determinations with compounds for which values have already been published.

Accordingly, calorimetric studies were made of fourteen nitro compounds

TABLE I

THERMOCHEMICAL CONSTANTS OF NITRO COMPOUNDS. HEAT OF COMBUSTION

Compound	G. cal. per g. at const. vol.	G. cal. per g. mole		Heat of formation at const. press.	Heat of nitration at const. press.
		At const. vol.	At const. press.		
Nitronaphthalene	6878.3	1,190,400	1,190,547	−7,147	49,750
1,5-Dinitronaphthalene	5298.9	1,155,521	1,154,641	−5,441	29,670
1,8-Dinitronaphthalene	5286.1	1,152,729	1,151,849	−2,649	31,400
1,3,8-Trinitronaphthalene	4223.9	1,111,181	1,109,275	+5,725	35,275
m-Nitraniline	5463.9	754,390	754,097	+17,503	54,500
	5552	766,500[2]	766,300[2]	+12,200	49,200
2,4-Dinitraniline	3933.9	720,179	718,859	+18,541	33,240
2,4,6-Trinitraniline	2962.2	675,595	673,249	+29,951	38,310
2,3,4,6-Tetranitraniline	2411.1	658,409	655,036	+13,964	10,910
p-Nitrophenol	4900.0	681,345	680,905	+56,500	47,000
			686,500[3]	+50,900	
2,4-Dinitrophenol	3526.7	649,096	647,629	+55,571	25,970
		650,200[3]	648,700[3]	+54,500	
2,4,6-Trinitrophenol (picric acid)	2687.2	615,514	613,021	+55,979	27,310
		623,700[3]	621,200[3]	+47,800	
	2677	613,200[4]	611,900[4]	+57,100	
2-Amino-4,6-dinitrophenol	3408.3	678,490	676,877	+60,523	
p-Nitrobenzaldehyde	5250.6	793,103	792,661	+44,139	
	5306	801,500[5]	801,000[5]	+30,800	
2,4,6-Trinitrobenzaldehyde	3035.0	731,599	729,106	+34,294	
2,4,6-Trinitrotoluene (TNT)	3598.9	817,202	815,296	+16,504	29,400
	3622	822,500[3]	820,700[3]	+11,100	
	3691	838,115[7]		+13,600[7]	
2,4,6-Trinitrophenylmethylnitramine (Tetryl)	2924.4	839,566	836,486	−4,686	14,100
		844,300[3]	842,300[3]	−10,500	
	3016.5[7]	866,007		−14,200[7]	
2,4,6-Trinitro-*m*-xylene (TNX)	4039.4	973,843	971,643	+22,907	
2,4,6-Trinitroresorcinol	2202.8	539,805	537,019	+131,981	
2,4,6-Trinitro-anisole	3236.1	786,599	784,399	+47,400	
2,4,6-Trinitrochlorobenzene	2609.4	645,842	643,202	−8,400	
Hexanitrodiphenylamine	3011.7	1,322,468	1,317,628	−13,828	
m-Dinitrobenzene	4149.4	697,315	696,342	+6,858	36,000
	4155	698,300[6]	697,200[6]	+6,000	
			699,400[3]	+3,800	33,000

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[2] Swarts, *Bull. acad. Belg.*, 43 (1909).

[3] Garner and Abernethy, *Proc. Roy. Soc. London*, **99A,** 213–235 (1921).

[4] Roth and Macheleldt, "Dissertation," Braunschweig, **1921.**

[5] Matignon and Deligny, *Compt. rend.*, **125**, 1103 (1897).

[6] Bertholet and Matignon, *ibid.*, **113,** 246 (1891).

[7] Rubtzov and Sever'yanov, *J. Russ. Phys.-Chem. Soc.*, **50,** 140–144 (1918).

for which no values were found in the literature, as well as of seven similar compounds of importance which had been studied by previous investigators. The data obtained are considered as serving to close a number of gaps in series of values available and hence of importance in determining the relationship between the constitutions and physical constants of chemical compounds.

Materials.—All materials used were of the highest purity, being purified by recrystallization until constant melting points agreeing with accepted values were obtained. Each compound was then kept in a sulfuric acid desiccator in a dark place until required for use.

Experimental Procedure.—A calorimeter of the Parr type was used in determining the values for heats of combustion given. This was equipped with a calibrated Beckmann thermometer and a cathetometer permitting the accurate estimation of 0.001°. The calorimeter was calibrated by means of pure benzoic acid furnished by the U. S. Bureau of Standards and found to give results accurate to ±11 calories per gram.

Duplicate or triplicate determinations were made with each material, the average value being reported. The initial temperature of the system in each case was 22 to 23°. Combustions were carried out with the oxygen in the bomb at a pressure of 400 lbs./sq. in. At the completion of each combustion the bomb was rinsed out and the nitric acid formed was determined by titration, the proper correction for this being applied to the calorimetric results.

Results.—The values for heats of combustion at constant volume were determined. From these the heats of combustion at constant pressure and the heats of formation were calculated. Table I gives the constants so determined and calculated, as well as a number of corresponding values reported by other investigators.

In making the calculations, the following constants were used: $R = 1.9885$; $T = 295°K.$; H_F of H_2O (liq.) = 68,400 cal./g. mole; H_F of CO_2 = 94,400 cal./g. mole; H_F of HNO_3 = 41,500 cal./g. mole.

A comparison of the values for heats of combustion determined with those previously recorded for some of the compounds would indicate a probable accuracy of about 1%. Standardization of the calorimeter indicated an accuracy of ±0.18%.

The possible error of 1% is based largely on the fact that Garner and Abernethy[3] give values from 0.2 to 1.3% (av. 0.7) higher for six compounds than those found by the writer. However, the value found for picric acid is 0.2% higher than that given by Roth and Macheleldt,[4] who also carried out their investigations quite recently. Rubtzov and Sever'yanov,[7] the only other recent investigators who have reported on two of these compounds, give results which apparently are much too high, being 2.5 and 3.1% higher than those determined by the writer and 1.9 and 2.6% higher than those reported by Garner and Abernethy. The work of the last-mentioned investigators having been done with great care, the results given by Rubtzov and Sever'yanov are at least open to question and do not form the basis of a fair comparison.

A similar comparison with values reported by other investigators shows that the determinations on check compounds herein reported are lower than those given by Swarts,[2] Matignon and Deligny[5] and Bertholet and Matignon[6] by 1.6, 1.4 and 0.1%, respectively.

From these facts it may be concluded that the new values for heats of combustion now reported have a possible error of −0.7%, though the existence of this percentage of error instead of the ±0.18% indicated by the calibration experiments cannot be considered as proved. The insufficiency of data giving direct comparisons with at least several other investigators for individual compounds renders doubtful any rigid conclusion that the results reported in this paper contain a consistent error approximating −0.70%. This lack of comparisons is due to the fact that the filling of gaps in existent data was the prime objective of this study.

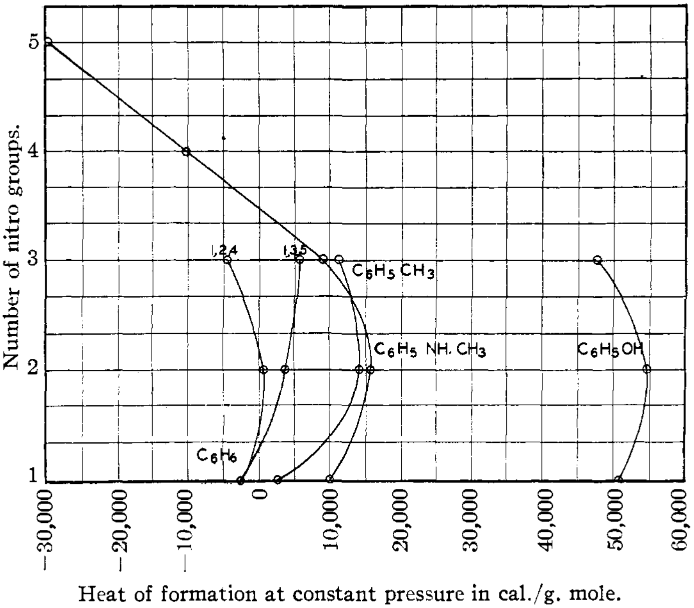

Fig. 1.

As is to be expected, when values for the heat of combustion of a compound determined by other investigators and the writer are used for calculating the heats of formation, the difference in results will be numerically equal but proportionally much greater than the difference in heat of combustion values. When the values for heats of formation of the compounds in each series of nitro derivatives, as calculated from the determinations of Garner and Abernethy[3] (Fig. 1) and of the writer (Fig. 2), are plotted against the number of nitro groups present in each compound, it is noted that the effect of the divergences is to produce curves having quite different orientations with respect to the reference axes.

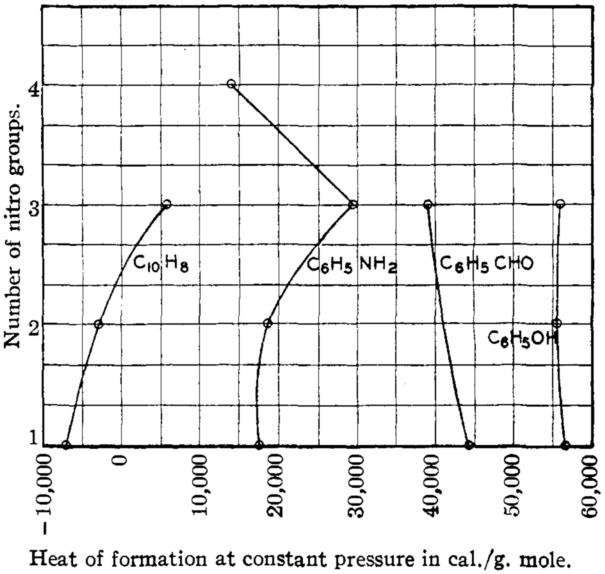

Fig. 2.

If the heat of formation be used to calculate the heat of nitration (reaction) evolved when each member of a nitro compound series is prepared by nitrating the next lower nitro compound or the hydrocarbon itself in the case of the mononitro compounds, comparative results having a bearing on the accuracy of the combustion values determined by the writer are obtained.

TABLE II

THERMOCHEMICAL DATA

	Heat of combustion at const. press.[a], cal./g. mole	Heat of formation at const. press., cal./g. mole	Heat of nitration, cal./g. mole
Nitrobenzene	739,700	−2,300	37,300
m-Dinitrobenzene	699,400	+3,800	33,000
1,3,5-Trinitrobenzene	663,400	+5,600	28,700
o-Dinitrobenzene	702,600	+ 600	29,800
1,2,4-Trinitrobenzene	673,700	−4,700	21,600
o-Nitrotoluene	897,200	+3,000	32,700
2,4-Dinitrotoluene	852,800	+13,200	37,100
2,4,6-Trinitrotoluene (TNT)	820,700	+11,100	24,000
p-Nitromethylaniline	924,300	+10,100	43,200
2,4-Dinitromethylaniline	884,500	+15,700	32,500
2,4,6-Trinitromethylaniline	857,900	+ 8,100	19,300
Tetryl	842,300	−10,500	8,300
p-Nitrophenol	686,500	+50,900	41,400
2,4-Dinitrophenol	648,700	+54,500	30,500
2,4,6-Trinitrophenol (picric acid)	621,200	+47,800	20,200

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%.

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[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

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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-

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[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.