tem extends into the $Na_2O-SiO_2-H_2O-CO_2$ system. However the correctness of this assumption will have to be checked by a more elaborate investigation of this system.

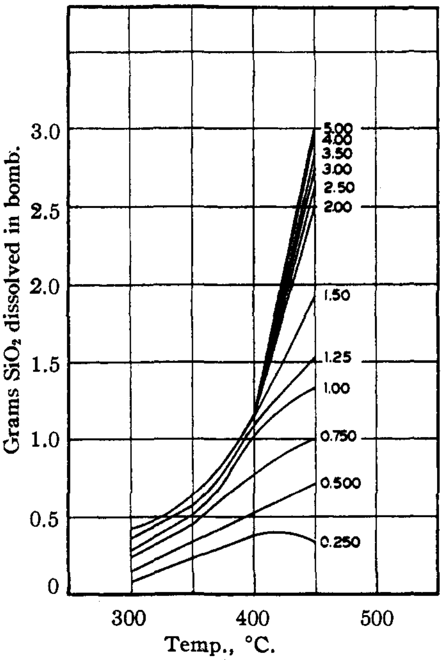

Fig. 2.

As can be seen from Fig. 2, this system would be a desirable one from which to grow quartz. The steep slope of the Solubility *vs.* Temperature curve would be favorable for growing quartz by the temperature lowering as previously stated, while the low solubility of quartz in sodium carbonate solutions as compared to its solubility in sodium hydroxide solutions, as shown in Table I, suggests that carbon dioxide might be used to displace quartz from sodium hydroxide solutions at constant temperature.

TABLE I

Temp., °C.	% Na_2O	Solubility, of quartz, g./l. NaOH solutions	Na_2CO_3 solutions
	1	20	5
300	5	135	28
	15	514	43
	1	25	13
350	5	152	50
	15	515	60
	1	35	22
400	5	155	90
	15	560	105
	1	35	24
450	5	163	124
	15	560	285

The author again wishes to emphasize the preliminary nature of the present paper. Much careful experimentation remains to be done before our understanding of equilibrium in multicomponent systems containing volatile and non-volatile components can be extended very far.

The assistance rendered by Mr. Charles Jackson was of great aid in carrying out the experimental work.

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[CONTRIBUTION FROM THE STAMFORD RESEARCH LABORATORIES, AMERICAN CYANAMID COMPANY]

Heats of Combustion of Some Organic Nitrogen Compounds

BY D. J. SALLEY AND J. B. GRAY[1]

The need for accurate values of heats of combustion for thermodynamic calculations has often been emphasized, and the lack of such data seems especially noticeable for organic compounds containing nitrogen. We therefore record here heats of combustion, determined with relatively high accuracy, of eight such compounds: cyanamide, dicyandiamide, melamine, 3-cyanopyridine, phthalonitrile, dimethylol urea, diisopropyl cyanamide, and diisopropyl carbodiimide.

Experimental

Apparatus and Procedure.—The bomb calorimeter used was modeled after that of Dickinson,[2] being a replica of that of Huffman and Ellis,[3] and of Richardson and Parks[4]; the calorimeter was in fact made in the shops of the California Institute of Technology.

The samples were burned in a Parr bomb (380 ml. capacity), containing initially 1 ml. of water and commercial tank oxygen at 30 atm. pressure at about 24°. The air was usually flushed out by two fillings with oxygen to 15 atm. pressure when solid samples were burned, but no flushing was made with liquids. The weight of water for the calorimeter, usually 2770 g., was measured to 0.05 g. on a high capacity balance.

Pellets of solid samples were weighed in a platinum crucible to 0.05 mg. on an analytical balance, after they had been kept in a desiccator over phosphorus pentoxide for several days. As far as is known, the compounds are not hygroscopic (except cyanamide, discussed below), and no changes in the heats of combustion with drying times of three to ten days were noticed. For liquids, thin-walled soft glass ampoules were completely filled by means of a fine hypodermic syringe, through a single stem, which was then sealed off. The liquids were not freed of any dissolved air.

Either of two methods of firing the sample have been employed, the platinum wire-string fuse of Richardson and Parks,[4] or the usual iron wire. In the former, the electrical energy (*EIT*) introduced was obtained by accurate measurements of voltage, current, and time. These

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[1] Present address: Guymon, Oklahoma.

[2] Dickinson, *Bull. Bureau of Standards*, **11**, 243 (1915).

[3] H. M. Huffman and E. L. Ellis, THIS JOURNAL, **57**, 41 (1935).

[4] J. W. Richardson and G. S. Parks, *ibid.*, **61**, 3543 (1939).

TABLE I

CALIBRATION OF CALORIMETER

Obs. rise, °C.	Cor. rise, °C.	Benzoic acid, wt. in vacuum, g.	Heat from benzoic acid, cal.	Heat from *EIT* + string, cal.	Heat from HNO_3, cal.	Energy equiv. cal./deg.	Dev. from mean cal./deg.
1.96923	1.97697	1.00010	6318.2	21.5	1.3	3207.4	+0.3
1.97121	1.97886	1.00102	6324.0	22.6	1.3	3207.9	+ .8
1.97270	1.98074	1.00179	6328.9	23.2	1.3	3207.6	+ .5
2.14473	2.15266	1.08907	6880.3	20.2	1.4	3206.2	− .9
1.97062	1.97856	1.00040	6320.1	23.9	1.3	3207.1	.0
1.86123	1.86878	0.94462	5967.7	24.3	1.3	3207.1	.0
2.13143	2.13995	1.08183	6834.6	25.8	1.3	3206.4	− .7

Mean = 3207.1 cal./g.

Calibration error = ±0.016%

were facilitated by an auxiliary circuit so arranged that on closing the switch to fire the charge the current reached a steady value within a small fraction of the firing time. Nearly identical current and time conditions were maintained from run to run, and the *EIT* introduced was checked frequently by direct measurement of the rise in temperature of the calorimeter in blank runs. The string, conditioned and weighed at 73° F. and 50% R. H., had a heat of combustion of 3950 calories per gram. The energy correction when an iron wire fuse was employed was determined by independent measurement of the temperature rise produced by the burning fuse alone in blank runs.

The temperature rise in the calorimeter was measured by a platinum resistance thermometer calibrated by the Bureau of Standards, a Mueller resistance bridge, and a high sensitivity galvanometer. A change of 0.00003 ohm (0.0003°) in the resistance of the thermometer caused a shift of 1 mm. in the reflection from the galvanometer mirror on the scale. The galvanometer was used as a null instrument, the time at which a predetermined resistance was reached being recorded on a drum-type chronograph which was precise to 0.1 sec.

Two methods of determining the corrected temperature rise have been employed, that described by Dickinson,[5] and that by Eckman and Rossini.[6] When using the former method, the jacket was at 25°, and in the latter at 26.1°. In either case the initial temperature of the run was so arranged that the average temperature of the combustion was 25 ± 0.1°. Jacket temperatures were maintained constant to at least 0.001°.

The nitric acid produced in the combustion was determined by titration with standardized alkali using brom cresol green as the indicator. The thermal correction was calculated on the basis of $\Delta H_R = -15{,}070$ cal./mole,[7] which yields 13,950 cal. evolved for one mole of aqueous acid formed in the bomb process. For all the nitrogen compounds the nitric acid correction was relatively high, 0.3 to 0.7% of the total heat involved, and a change of 1000 cal. in the value of 13,950 cal. for nitric acid formation can effect changes of 0.02 to 0.05% in the final figures for the heats of combustion.

Units.—The unit of energy used is the defined calorie = 4.1833 int. joules. The unit of mass is the gram true mass derived from the weight in air against brass weights. The appropriate buoyancy correction depends on the density of the substance and this was obtained from the literature or measured independently. 1947 atomic weights[8] were used in calculating molecular weights.

Calibration.—The calorimeter was calibrated by burning benzoic acid (Bureau of Standards standard sample 39f; heat of combustion 26.4284 int. kj./g.) under conditions meeting as closely as possible the standard calorimetric conditions specified by the Bureau of Standards. Deviations from the specifications were so small as to require an entirely negligible change (0.003%) in the NBS value for the benzoic acid. Table I presents some early determinations which were carried out using the platinum wire-string fuse for firing, and the Dickinson procedure for correcting the temperature rise. The figures recorded are the experimental values of the energy equivalent of the bomb and contents. These runs give an indication of the precision of the experimentation; the calibration error shown is calculated according to Rossini.[9] Numerous calibrations made from time to time have shown an even better degree of precision. No marked advantage in precision has been found between the various procedures tested.

Materials.—All of the compounds were purified by various members of these Laboratories or of the Calco Chemical Division of the American Cyanamid Company, and analyses were made by our Analytical Department. Nitrogen analysis was obtained in several instances, but since it is not a very good criterion of purity with these compounds, whenever possible, analytical procedures or other means of characterization specific for the compound in question were employed.

Cyanamide.—Free cyanamide was recrystallized from ether, then vacuum distilled at whatever pressure was obtainable with a mercury pump when the melt was held at 80° and the distillate was trapped at 0°. Ampoules of the material, filled as described in the following, showed only a trace of dicyandiamide, the only likely impurity.

The handling of cyanamide deserves special mention. This material is a solid melting at about 41°, but its hygroscopic and corrosive nature precludes pelleting. However, its low melting point allowed it to be handled as a liquid. The door of an electric oven was fitted with two sleeves ending in rubber gloves. Trays of Drierite and Ascarite were placed in the oven to absorb water vapor and carbon dioxide. The temperature was kept at 50–60°. A hypodermic syringe and glass ampoules were placed in the oven several hours before use. The cyanamide, in an evacuated flask, was melted rapidly under a steam jet, then opened inside the oven. A glass tube having a fitted ground joint was substituted for the needle, and the molten material quickly drawn into the syringe; the needle was then replaced for filling the ampoules. Since the rather high viscosity of the melt made the expulsion of the liquid through the fine needle difficult, it was convenient to clamp the syringe firmly in a small stand which also carried a small adjustable platform on which the ampoule rested. After filling all the ampoules they were removed from the oven one by one and sealed off. Since supercooling often took place, each bulb was chilled with a piece of ice to induce crystallization. In the molten state cyanamide converts slowly to dicyandiamide so that all the operations were carried out as rapidly as possible. To insure consistent firing of these samples

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(5) H. C. Dickinson, *Bull. Bureau of Standards*, **11**, 189 (1914).

(6) J. R. Eckman and F. D. Rossini, *Bur. Standards J. Research*, **3**, 597 (1929); Rossini, *ibid.*, **6**, 1 (1931).

(7) Tables of Selected Values of Chemical Thermodynamic Properties. Series I, Table 8-1 and 18-6, National Bureau of Standards, March 31, 1947.

(8) G. P. Baxter, M. Guichard and R. Whytlaw-Gray, *J. Chem. Soc.*, **983** (1947).

(9) F. D. Rossini, *Chem. Rev.*, **18**, 235 (1935).

when using the iron wire method, small weighed disks of filter paper (0.011–0.012 g.; heat of combustion, 3992 cal./g.) were stuck to the ampoule by a tiny smear of water glass. This technique of handling hygroscopic solids has been used satisfactorily with other such materials of sufficiently low melting point.

Dicyandiamide.—Commercial material was twice recrystallized from water. Nitrogen analysis showed 66.54%, indicating a purity of 99.82%.

Melamine.—This sample was purified by recrystallization from dilute sodium hydroxide. Specific analysis for melamine showed it to be 99.7% pure, free of ammeline and ammelide, with less than 0.01% ash.

3-Cyanopyridine.—This compound, prepared from 3-bromopyridine by reaction with cuprous cyanide, was twice redistilled. The product of the second distillation boiled constantly at 98° at 23 mm. and melted at 49–50°. The nitrogen analysis was: found 26.66%, theoretical 26.90%.

Phthalonitrile.—A commercial material was purified by recrystallization from alcohol; m. p. 138.5–140°. Nitrogen analysis was 21.65% *versus* 21.87% theoretical.

Dimethylol Urea.—This compound was recrystallized from 75% alcohol. It showed a m. p. of 137–139° with decomposition. Nitrogen analysis was 23.18% found, 23.33% theoretical.

Diisopropyl Cyanamide and Diisopropyl Carbodiimide.—Both of these compounds were purified by several fractional distillations. The former boiled at 75° at 5 mm., the sample being a middle cut. The latter boiled at 25 mm., a middle cut being taken; infrared examination showed that it conformed to other samples of high purity.

Data

As a typical example, Table II presents the experimental data for the heat of combustion runs on melamine. The Rossini method of correcting for the temperature rise was followed in this case, K and U being the heat leak corrections. The calorimeter calibration had also been done using this method. ΔR_i is the ignition correction (*EIT* and string), and ΔR_n is the correction for the nitric acid formed. These quantities as well as the temperature rise R, are in ohms, while the energy equivalent obtained in calibration runs is stated in cal. per ohm. The quantity, $-\Delta U_{B/m}$, in this and the following table, represents the heat evolved per gram in the isothermal bomb process at 25°. Correction to the isothermal reaction using known or estimated specific heats was negligible, being in all cases less than 0.01%.

In Table III there are collected the data on the eight compounds burned. The headings are self-explanatory, except perhaps that of the seventh column. This is the "precision error" calculated using an assigned error of 0.010% for the heat of combustion of benzoic acid, a "calibration error" of 0.016%, and the "reaction error" that obtained in each case. The Washburn correction[10] involved in calculating ΔU_R was derived on the basis that the ternary mixture of nitrogen, oxygen, and carbon dioxide behaved like the binary mixture, oxygen and carbon dioxide; we are indebted to Mr. A. B. Bestul for these calculations. The heats of formation of the compounds from the elements, ΔH_f, were calculated using 94,051.8 and 68,317.4 cal./mole for the heats of formation of gaseous carbon dioxide and of liquid water,[11] respectively.

TABLE II

DATA ON HEAT OF COMBUSTION OF MELAMINE

Wt. in vacuum, g.	ΔR obs., ohm	K, ohm $\times 10^1$	U ohm $\times 10^4$	ΔR_i ohm $\times 10^4$	ΔR_n, ohm $\times 10^3$	ΔR corr., ohm	$-\Delta U_{B/m}$ cal., g.
1.71222	0.20620	2.545	4.97	7.00	1.194	0.20126	3735.2
1.70679	.20540	2.472	3.71	7.29	1.215	.20061	3735.0
1.71574	.20700	2.538	9.13	6.94	1.173	.20168	3735.4
1.70903	.20560	2.456	2.30	7.87	1.150	.20098	3736.9
1.71390	.20620	2.459	3.48	6.64	1.180	.20155	3736.9
1.71530	.20630	2.425	2.02	6.87	1.252	.20173	3737.2
							Mean 3736.1

Reaction error ±0.021%: precision error ±0.028%. Energy equivalent of calorimeter 31777.1 cal./ohm.

TABLE III

HEATS OF COMBUSTION AND FORMATION AT 25°

Substance	Formula	Mol. wt.	Density	No. of runs	$-\Delta U_{B/m}$, cal./g.	Prec. err., %	$-\Delta U_R$, kcal./mole	$-\Delta H_R$, kcal./mole	ΔH_f, kcal./mole
Cyanamide(s)	CH_2N_2	42.042	1.282	6	4206.4	0.069	176.72	177.20	14.65
Dicyandiamide(s)	$C_2H_4N_4$	84.084	1.40	4	3943.1	.036	331.29	331.88	7.14
Melamine(s)	$C_3H_6N_6$	126.126	1.573	6	3736.1	.028	471.22	471.76	− 15.35
3-Cyanopyridine(s)	$C_6H_4N_2$	104.108	1.159	4	7181.4	.027	747.14	747.73	46.78
Phthalonitrile(s)	$C_8H_4N_2$	128.128	1.125	4	7457.3	.025	954.81	955.40	66.35
Dimethylol urea(s)	$C_3H_8N_2O_3$	120.110	1.49	4	3202.0	.043	384.34	384.64	−170.78
Diisopropyl cyanamide(l)	$C_7H_{14}N_2$	126.198	0.949	7	8899.9	.066	1122.81	1124.88	− 11.70
Diisopropyl carbodiimide(l)	$C_7H_{14}N_2$	126.198	0.909	5	8958.0	.051	1130.14	1132.21	− 4.37

Discussion

The precision of the calorimetric procedure, as indicated by the calibration runs, appears to be entirely satisfactory. This is further borne out by the fact that equally good results have been obtained with other non-nitrogen compounds (not published). However, the results with the nitrogen materials have never reached the same precision. This may have been due to irregularities in the course of the combustion process. Some support for this view is provided by the fact that ignition difficulties were often encountered, and that incompleteness of combustion (as evidenced by carbon deposition) was rather frequent. It seems evident that to obtain highest precision the combustion process for nitrogen compounds would require detailed study, and that direct determination of carbon dioxide and the nitrogen oxides

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[10] E. W. Washburn, *Bur. Standards J. Research*, **10**, 525 (1933).

[11] D. D. Wagman, J. E. Kilpatrick, W. J. Taylor, K. S. Pitzer and F. D. Rossini, *J. Research Natl. Bur. Standards*, **34**, 143 (1945).

would be necessary. In the present work, no direct test for completeness of combustion by measurement of carbon dioxide or carbon monoxide formation was made on any of the compounds.

The accuracy of the values reported here is almost certainly poorer than the precision of the determinations, since the purity of the samples—in spite of the effort to obtain high-grade materials—probably is the limiting factor. The compounds were all taken as 100% pure even though in some instances the analysis throws some doubt on this, and in the case of the liquids no attempt was made to correct for any dissolved gases. This appears to be the best policy to follow, first, because the significance of the analysis may be questioned and, second, because the kind and amount of impurity is indeterminate. The cyanamide, dicyandiamide and melamine figures are considered to be the most reliable in this respect.

The heats of combustion of cyanamide, dicyandiamide and melamine were measured by Lemoult,[12] his figures being 171.6, 328.7 and 469 kcal./mole, respectively. These values are nominally 5.6, 3.2 and 2.8 kcal./mole lower than those obtained here. Since the corresponding heats of formation have rather low absolute values, these differences naturally result in large percentage differences between the old and new heats of formation. The present values are considered to be the more trustworthy. No values have been located in the literature for the other substances.

Acknowledgment.—Acknowledgment is made to Mr. P. Adams, Dr. P. R. Averell, Dr. I. Heckenbleikner, Dr. R. F. Stamm, and members of the Analytical Department of these Laboratories for the preparation, purification, and analysis of the compounds used, and to the Directors of these Laboratories for permission to publish these results.

Summary

A bomb calorimeter, calibrated with benzoic acid, has been used for determining the heats of combustion of eight organic nitrogen compounds at 25° and constant volume. From these data, the corresponding heats of combustion and of formation at constant pressure have been calculated. The substances burned were cyanamide, dicyandiamide, melamine, 3-cyanopyridine, phthalonitrile, dimethylol urea, diisopropyl cyanamide, and diisopropyl carbodiimide.

STAMFORD, CONN. RECEIVED MARCH 30, 1948

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(12) P. Lemoult. *Ann. chim. phys.*, [7] **16**, 338 (1898). See also F. R. Bichowsky and F. D. Rossini. "Thermochemistry of Chemical Substances." Reinhold Publishing Corp.. New York. N. Y.. 1936. p. 50.

[CONTRIBUTION FROM THE STAMFORD LABORATORIES OF THE AMERICAN CYANAMID CO.]

Some Amides and Esters of Fluoroacetic Acid

BY J. C. BACON, C. W. BRADLEY,[1] E. I. HOEGBERG, PAUL TARRANT[2] AND J. T. CASSADAY

The toxicity of certain derivatives of fluoroacetic acid to insects and rodents was established in these Laboratories several years ago and has led to the synthesis of additional compounds of this type.

The problem of preparing economically a simple derivative of α-fluoroacetic acid to be used as a starting material for the rest of these syntheses was solved by the discovery of a method for converting chloroacetamide into fluoroacetamide by reaction with potassium fluoride. This method is discussed below. The literature[3-5] has subsequently indicated that during the course of our investigations methods were simultaneously in the process of development in England, Poland, and elsewhere in the United States for the large-scale production of methyl, ethyl and sodium fluoroacetates, the latter being known as rodenticide "1080." Analytical methods have been reported[4] for the determination of extremely small traces of fluorine in these and similar types of materials and reports[6,7] have also been published covering the effect of "active" fluorine compounds on warm-blooded animals.

Numerous unsuccessful attempts were made to replace the chloro group of chloroacetic acid and ethyl chloroacetate using hydrogen fluoride alone or in combination with antimony trifluoride.

Fluoroacetamide was finally prepared by the reaction of chloroacetamide with potassium fluoride. A mixture of the fluoro- and chloroamides was obtained both by dry distillation under reduced pressure and by distillation at atmospheric pressure using xylene as a carrier. The yields of fluoroacetamide based upon the chloroacetamide consumed were greater than 50%. The mixture of amides was converted into a

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(2) Present address: University of Florida. Gainesville. Florida.

(3) H. McCombie and B. C. Saunders. *Nature*. **158**, No. 4011. 382 (1946).

(4) W. B. Reed for R. L. Jenkins and E. E. Hardy. Office of Technical Service Report. PB 24903; C. W. Mason and C. B. De La-Mater. PB 5484; J. H. Yoe. Jason M. Salsbury and James W. Cole. PB 5955. PB 4220. PB 6020. PB 6021; John H. Yoe and Lyle G. Overholser. PB 4216; Benjamin Witten. Bernard Gehauf and Melvin M. Falkof. PB 17207; Joseph M. Sanchis. PB 9511; Irving S. Goldman. Mary Catherine Flannery. Louis J. Arent. John B. Hoag. Arthur M. Buswell. PB 9510; Charles C. Price and William G. Jackson. PB 5904; Nathan L. Drake. PB 5863. R. H. Kimball and Lewis E. Tufts. PB 52707.

(5) E. Gryszkiewics-Trochimowski. A. Sporzynski and J. Wnuk, *Rec. trav. chim.*. **66**. 413–418 (1947).

(6) Maynard B. Chenoweth and Alfred Z. Gilman. PB 9577; Sidney P. Colowick. Louis Berger and Milton W. Slein. PB 5873.

(7) Marais and Onderstepoort. *J. Vet. Sci. Animal Ind.*, **18**. 203 (1943); **20**, 67 (1944).