Heats of Combustion and Heats of Formation of 3,4-Dicyanofuroxan, 3,4-Dicyanofurazan, and Sesquimer of 3,4-Dicyanofuroxan

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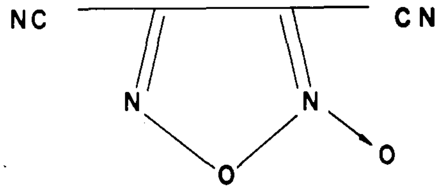
Thermochemical values determined by bomb combustion calorimetry are reported for the compounds 3,4-dicyanofuroxan (DCFO), 3,4-dicyanofurazan (DCFA), and DCFOB. DCFOB is a sesquimer of DCFO of molecular formula $C_6N_6O_3$. Reference is made to the toxicity of all three compounds. An ignition system for measuring energy released during combustion is described.

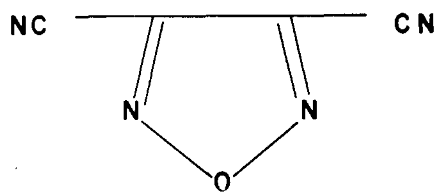
The heat of formation of a compound is an important quantity for calculating combustion properties. In particular, the heat of formation is required to calculate the specific impulse of a chemical rocket propellant (a measure of its efficiency) and to calculate the temperature of combustion (*8*). Consequently, determination of the heat of formation is a required step in characterization of propellants for rockets and for rocket-like combustors, such as some lasers.

The construction of one type of combustion-powered gas dynamic laser requires a storable, noncryogenic fuel which gives as combustion products CO_2, CO, N_2 in specific proportions and H_2O in the range 1–2%. Those organic compounds which contain no hydrogen might be suitable for the fuel mixture; however, only a few compounds containing only C, N, O, and no H are known, and thermochemical data for these compounds are even more rare. This paper reports the determination of heats of combustion and heats of formation of three candidate fuels for a rocket-driven chemical laser which contain only C, N, and O: 3,4-dicyanofuroxan (DCFO, I, $C_4N_4O_2$):



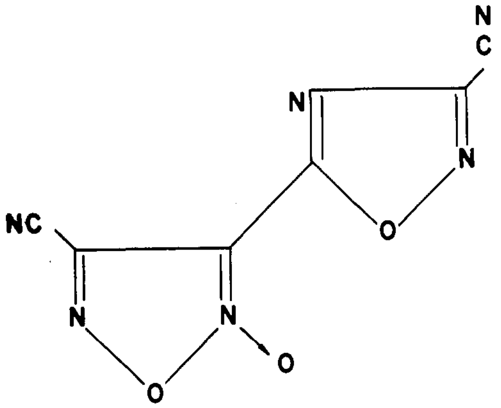
I

3,4-dicyanofurazan (DCFA, II, C_4N_4O):

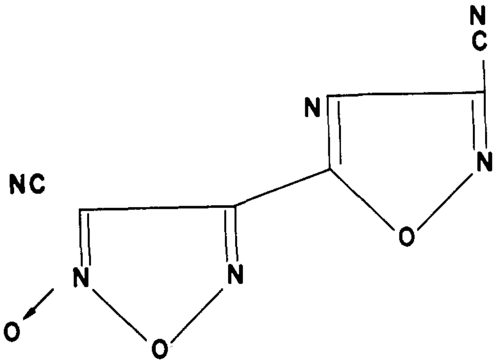


II

and a sesquimer (1½ mer) of 3,4-dicyanofuroxan of uncertain structure (DCFOB, $C_6N_6O_3$). The most likely structures for the sesquimer are given below (III and IV) (*4*):



III



IV

Experimental

Apparatus. A precision Scientific Equipment Model 63090 combustion calorimeter was used for these measurements. An additional propeller was attached to the inside can stirring shaft to provide adequate mixing. A Parr Model 1106 platinum-lined inverted combustion bomb was used, since we discovered that when a Parr 1105 Model (right side up) bomb was used, charring of the sealing rubber gasket resulted. A Hewlett-Packard Model 2801A quartz digital thermometer was used to measure the temperature rise of the combustion. Since the instrument specifications claim that the quartz thermometer reading changes 0.003°C for every 1°C temperature change in the electronics box, the temperature of the electronics box was controlled. A thermistor was placed inside the electronics box, connected to an RFL Inc., proportional controller, and the output of the proportional controller was used to power a heating tape which covered the air inlet vent of the electronics box. The electronics box was maintained about 5°C above its normal operating temperature (45°C). The use of temperature control on the digital thermometer electronics box improved the precision of benzoic acid standardization runs by a factor of 20.

Volume of the bomb is 390 ml, and 3 ml of water was added to the bomb. The samples were pelletized and

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burned in a platinum crucible and were not encapsulated. Platinum fuse wire was used to initiate combustion, and no auxiliary material was used. The value of the calorie was considered to be 4.184 J. Enthalpies of formation used for combustion products were: H_2O (−68.32 kcal/mol), CO_2 (−94.05 kcal/mol) (7). A value of 59.43 kJ/mol was used to correct combustion energy values for the formation of 0.1 in nitric acid in the bomb (3). Densities and heat capacities used for the compounds are listed in Table I.

Ignition system. An ignition system was designed using a large capacitor in which a circuit measured the power delivered by the capacitor and when the fuse wire burned through, triggered a relay to disconnect the capacitor. A circuit diagram of this automated ignition system is available on request from the authors.

Data analysis. The computer program used to reduce our calorimetric data has been reported elsewhere (3). A copy of the program is available upon request from the authors. The program, as previously published, was modified to accept data from the quartz digital thermometer, which was set to measure temperatures accurate to 0.001°C, printing one temperature value every 15 sec.

Compounds. The 3,4-dicyanofuroxan was prepared according to the manner of Merrill and Barnes (5) and the method of Parker et al. (6), and the 3,4-dicyanofurazan was prepared by reduction of DCFO and by a four-step synthesis (4). The sesquimer of 3,4-dicyanofuroxan was a by-product in the synthesis of 3,4-dicyanofuroxan. Note that all of these compounds are very toxic, both upon inhalation and cutaneous contact (1). In addition, they react explosively with hydrazines.

Purity of compounds. NBS certified benzoic acid could not be obtained in time for these measurements; therefore, Parr calorimetric grade benzoic acid pellets were used to standardize the calorimeter. Baker analyzed reagent grade hippuric acid was recrystallized from water, dried in a vacuum dessicator, and used as a secondary standard. The 3,4-dicyanofuroxan was purified by recrystallization from CCl_4 and by vacuum sublimation. Both 3,4-dicyanofuroxan and 3,4-dicyanofurazan showed only one peak upon vapor-phase chromatography (silicone oil column). Melting-point depression suggested that DCFO contained a very small amount (0.1%) of DCFOB, but the heat of combustion of DCFOB is so similar on a weight basis to that of DCFO that negligible error was caused by the presence of this minor impurity. DCFOB was recrystallized from 1,2-dichloroethane to constant melting point 90–91°C.

Table I. Densities and Heat Capacities of Calorimetric Samples

Compound	g/ml	c_p (25°, J/g-°C)
BA	1.32[a]	1.09[a]
DCFO	1.52[b]	0.71[b]
DCFA	1.52[b]	0.71[b]
DCFOB	1.52[b]	0.71[b]
HIP	1.37[c]	1.19[d]

[a] These values are reported by the U.S. National Bureau of Standards for benzoic acid. [b] The values for DCFO were determined in our laboratory by M. F. Citro, R. Avanzino, and T. W. Owens. The DCFO values were also used for DCFA and DCFOB. [c] "Handbook of Chemistry and Physics," 47th ed., Chemical Rubber Co., Cleveland, Ohio, 1966. [d] This value is estimated.

Table II. Summary of Calorimetric Results

Compound	$\Delta H°_{comb}$ (25°, s) kcal/mol	$\Delta H°_f$ (25°, s) kcal/mol
DCFO	−487.47 ± 0.2	+111.3 ± 0.2
DCFA	−485.1 ± 1.3	+109.0 ± 1.3
DCFOB	−699.4 ± 1.0	+135.1 ± 1.0

Results

Table II summarizes the calorimetric results, and Table III lists typical values of the combustion parameters. In each case, the value reported is the mean of all runs which were performed. The number of runs performed are in parentheses after the compound identification. Only two DCFA measurements were made because very little compound was available.

The reactions to which the quantities in Table I correspond are:

DCFO combustion

$$C_4N_4O_2 + 3O_2 \rightarrow 4CO_2 + 2N_2$$

DCFO formation

$$4C(s) + 2N_2 + O_2 \rightarrow C_4N_4O_2$$

DCFOB combustion

$$C_6N_6O_3 + 4\tfrac{1}{2}O_2 \rightarrow 6CO_2 + 3N_2$$

DCFOB formation

$$6C(s) + 3N_2 + 1\tfrac{1}{2}O_2 \rightarrow C_6N_6O_3$$

DCFA combustion

$$C_4N_4O + 3\tfrac{1}{2}O_2 \rightarrow 4CO_2 + 2N_2$$

DCFA formation

$$4C(s) + 2N_2 + \tfrac{1}{2}O_2 \rightarrow C_4N_4O$$

Because of a modification made to the calorimeter in the middle of these experiments, there are two values for the energy equivalent of the calorimetric system. The experiments are divided into two series, A and B, depending on which energy equivalent is used. Mass is the mass of the compound in vacuo. ml_{NaOH} is the volume of 0.1059*N* NaOH solution required to titrate the acid formed during combustion to a phenolphthaleim end point. E_{ign} is the electrical energy dissipated during ignition. T is the corrected temperature rise during combustion. T_{max} is the temperature at the end of the combustion period. E_s is the energy equivalent of the system.

The error limits expressed in Table I are the standard deviations of the values obtained. The error limits in Table II are calculated by the formula:

$$\frac{(\text{Error limit})^2}{(H°_{comb})^2} = \frac{T^2{}_{es}}{E^2{}_s} + \frac{T^{2°}{}_{e\,comb}}{(E°_{comb})^2}$$

The International atomic weight scale of 1959 was used. Hippuric acid was burned as a secondary standard. Combing the Series A and Series B results, $H°_{comb}$ (25°, s) = −1006.48 ± 1.1 kcal/mol (this error limit is calculated as were the limits in Table II). This compares with a value of −1008.35 ± 0.39 kcal/mol obtained by Hubbard et al. (2).

Although DCFO, DCFA, and DCFOB might decompose very exothermally upon ignition, there was no indication of incomplete combustion. No carbon was found in the bomb, and mass spectral analyses of combustion products showed no HCN or $(CN)_2$, and CO < 0.0001 CO_2.

Table III. Calorimetric Parameters

Compound	Series	Mass, g	ml_{NaOH}	E_{ign}, J	T, °C	T_{max}	E_s, J/°C
			Standardization				
BA (6) (benzoic acid)	A	1.120314	5.92	6.51	1.48809	25.75	19929.7 ± 3.7
BA (6)	B	1.067590	5.94	7.83	1.41630	26.62	19956.5 ± 4.5
							E°_{comb}, J/g
			Determination				
DCFO (6)	A	1.427027	13.17	7.00	1.08324	25.89	15043.2 ± 7.4
HIP (1) (hippuric acid)	A	0.909139	8.03	7.39	1.07628	26.48	23482.3
DCFOB (4)	B	1.278989	12.01	7.44	0.92769	25.79	14349.2 ± 20.9
DCFA (2)	B	1.300227	12.76	6.68	1.11257	26.25	16935.4 ± 46.0
HIP (1)	B	1.213106	10.50	7.28	1.432216	26.57	23452.7

Quality of Data

As seen from the precision of benzoic acid sort standardization data, our calorimetric system is capable of producing research quality data (±0.02%). However, it was intended for this project that good quality calorimetric data would be obtained as part of the characterization program; then, if one or more compounds were selected as storable fuels for the gas dynamic laser, research quality data would be determined for that compound or compounds. Unfortunately, all of the compounds here reported were, for one reason or another, excluded from consideration before research quality data were required.

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Equilibrium Vapor Pressures and Vapor-Phase Dissociation of Monoammine of Aluminum Chloride

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The vapor pressures in equilibrium with liquid NH_3AlCl_3 and equilibrium constants for the vapor-phase dissociation of the ammine into ammonia and aluminum chloride are studied in Pyrex diaphragm gauge experiments. An enthalpy of formation of −190.5 kcal mol^{-1} and a standard entropy of 85.0 cal mol^{-1} deg^{-1} are derived for $NH_3AlCl_3(g)$ at 25°.

This work was undertaken to establish the vaporization thermodynamics of the monoammine of aluminum chloride, NH_3AlCl_3. In addition to an inherent interest in these properties, the information was needed as part of a more general study of the vaporization characteristics of the complex compound ammonium tetrachloroaluminate. A substantial amount of information about the ammoniates of aluminum chloride has been published (*4*). Klemm and collaborators (*7, 8*) report compounds containing 1, 3, 5, 7, and 14 moles of ammonia, respectively, for each mole of aluminum chloride. They report a heat of formation for the monoammine, based on heat of solution experiments; this value, together with the low melting point, 125°, and relatively large molar volume of the solid, is said to be suggestive of a molecular lattice. Vapor-pressure data for the liquid, determined from diaphragm gauge and transpiration studies, were reported; dissociation of the ammine in the equilibrium vapor phase was estimated to be less than 1% below 400°.

Results of a more recent study of the equilibrium vapor pressure have been reported by Yurlova and coworkers (*14*) and do not agree well with those of Klemm et al. The present work was undertaken in part to resolve this discrepancy. We have measured vapor pressures in equilibrium with the liquid phase in a Pyrex diaphragm gauge; pressures developed by a known quantity of the unsaturated vapor indicate a slight dissociation of the ammine into ammonia and aluminum chloride. Apparent equilibrium constants for the dissociation reaction have been derived and used to evaluate thermodynamic properties of $NH_3AlCl_3(g)$.

Experimental

Samples were studied in a Pyrex envelop containing a thin Pyrex membrane as a pressure-sensing device (*1*).

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