zero at long times, as shown in Figure 6. In addition, the relaxation spectra calculated from G_{1r} and G_{2r} data show qualitative agreement with each other, in that both curves have the same shape (a linear relation between log H and log τ). However, since the magnitudes of the spectra are different, quantitative conclusions are less reliable. The quantitative difference in the curves is understandable considering errors inherent in calculating G_{1r} from experimental data obtained in this study compared to errors in calculating G_{2r}.

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Energy of Combustion and Differential Thermograms of Organic Azides

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The heats of formation of two series of triazoles, 3-azido-*s*-triazoles, I, and 4-amino-3-azido-*s*-triazoles, II, are reported from the heats of combustion in an oxygen bomb calorimeter. Differential thermograms were also obtained to determine the thermal stability of each compound.

THE ENERGY CONTENT of a chemical compound is of major importance in the evaluation of its potential as a propellant ingredient. As a part of a program to synthesize and measure physical properties of energetic compounds, the heats of combustion and formation of two series of triazoles, 3-azido-*s*-triazoles, I, and 4-amino-3-azido-*s*-triazoles, II, were determined. Differential thermograms were also obtained on these compounds to determine their thermal stability.

Although the heats of combustion of few organic azides (*1, 2, 6*) have been described, the energy contents of high nitrogen heterocyclic azides have not been reported. The paucity of such information is undoubtedly due to the difficulty in synthesis and the ease with which these compounds decompose during the purification process. The problem of synthesis has been circumvented by the initial preparation of the hydrazinotriazoles and their subsequent conversion to the corresponding azidotriazoles.

EXPERIMENTAL

Materials. The 3-azido-*s*-triazoles, I, and 4-amino-3-azido-*s*-triazoles, II, were prepared by treatment of the corresponding 4-amino-3-hydrazino-*s*-triazole hydrochlorides (*3, 8, 9*) with 2 and 1 equivalents of nitrous acid, respectively. The azides prepared in this manner are listed in Table I. A representative example for each is given below.

3-AZIDO-*s*-TRIAZOLES. A solution of 8.9 grams of sodium nitrite in 15 ml. of water was added dropwise to an ice-cold solution of 9.0 grams of 4-amino-3-hydrazino-*s*-triazole hydrochloride in 65 ml. of 2*N* hydrochloric acid. When half of the nitrite had been added, a precipitate appeared

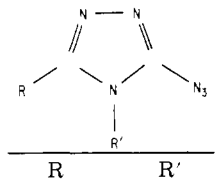


Table I. Azido-s-triazoles[a]

No.	R	R′	M.P., °C.[b]	Formula	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	Nitrogen, % Calcd.	Nitrogen, % Found
Ia	H	H	120–21.5	$C_2H_2N_6$[c]	21.82	21.60	1.83	2.40	76.34	76.35
Ib	CH_3	H	143–45	$C_3H_4N_6$	29.03	29.18	3.25	3.46	67.72	67.57
Ic	C_2H_5	H	116.5–19	$C_4H_6N_6$	34.78	34.74	4.38	4.62	60.84	60.85
Id	C_6H_5	H	191–92 dec.	$C_8H_6N_6$	51.61	51.69	3.25	3.44	45.14	45.36
IIa	H	NH_2	52–55 dec.	$C_2H_3N_7$	19.20	18.82	2.42	2.59	78.38	78.38
IIb	CH_3	NH_2	84–86 dec.	$C_3H_5N_7$	25.90	25.78	3.63	3.90	70.48	70.31
IIc	C_2H_5	NH_2	81–83 dec.	$C_4H_7N_7$	31.37	31.61	4.61	4.89	64.02	64.06
IId	C_6H_5	NH_2	150–51 dec.	$C_8H_7N_7$	47.75	47.71	3.51	3.52	48.73	48.72

[a] Analyses performed in this laboratory. [b] All melting points uncorrected. [c] Samples detonated, breaking combustion tubes during analyses, and good values for hydrogen could not be obtained.

and the yellow mixture started to foam. The remainder of the nitrite solution was cautiously added, and then the mixture was allowed to warm up to room temperature. The yellow solid was collected by filtration after neutralization of the mixture with sodium carbonate to pH 9 to 10. An additional product was collected by extraction of the filtrate with ether to yield a total of 5.40 grams (81%) (m.p. 114–18° C.). Recrystallizations from benzene gave an analytical product (m.p. 120–21.5° C.).

4-AMINO-3-AZIDO-5-ETHYL-*s*-TRIAZOLE. A solution of 4.2 grams of sodium nitrite in 10 ml. of water was added dropwise to an ice-cold solution of 10.68 grams of 4-amino-5-ethyl-3-hydrazino-*s*-triazole hydrochloride in 30 ml. of 2*N* hydrochloric acid and 35 ml. of water. After stirring in the cold for 15 minutes, the mixture was allowed to warm to room temperature. The reaction mixture was neutralized carefully with sodium carbonate to pH 9 to 10 and then extracted with ether on a continuous extractor for 72 hours. The pink-colored ethereal solution was dried over calcium sulfate, and the solvent was removed under vacuum to yield 7.77 grams (84.5%) of pinkish white solid (m.p. 78–82° C., decomposed). The solid was triturated with ether to remove the pink color and repeatedly dissolved in tetrahydrofuran and precipitated by the addition of ligroine (b.p. 60° to 90° C.). The white crystals (m.p. 80–83° C., decomposed) obtained were dried under vacuum at room temperature. The product turned light pink on exposure to light or on long standing in air.

Calorimetry Apparatus and Procedure. The heats of combustion were determined using a Parr (Series 1200) adiabatic bomb calorimeter, surrounded by a constant temperature bath controlled to ±0.02° C. Temperature measurements were made with a platinum resistance thermometer and a Leeds and Northrup G-2 Mueller bridge to ±0.0005° C. The bomb was flushed once with 30 atm. of oxygen and then filled to this pressure. One milliliter of water was placed in the bomb before ignition. Samples were prepared as 0.5-inch diameter pellets. For the calibration work, 1-gram samples of NBS benzoic acid were used. Six calibrations of the calorimeter were made before and during these combustion experiments. The heat capacity of the calorimeter and the standard deviation was 24,307 ±14 cal. per ohm. To promote the combustion of the triazoles, benzoic acid was used as an igniter. Varying the amount of benzoic acid, sample size, and pelletizing pressure did not ensure complete combustion. Traces of carbon or thin oily films were found in the sample crucible after most of the firings. Where this residue exceeded 0.25 weight % of the triazole sample, the run was discarded. Smaller residues were treated as unburned carbon and a correction of 7830 cal. per gram was made. Exhaust gases from the bomb were checked for carbon monoxide by gas chromatography; none was found. The average over-all temperature rise of the calorimeter was 2° C.

Table II. Combustion Data

Compound	Mol. Wt.	Sample Wt., G.	Benzoic Acid Wt., G.	ΔE_c, Kcal./Mole	ΔH_f, Kcal./Mole	σ
Ia	110.086	0.62206	0.32143	362.85	105.52	0.81
		0.67085	0.33014	363.98		
			Av.	363.42		
Ib	124.113	0.60989	0.38138	513.98	93.84	1.21
		0.67245	0.30983	514.91		
		0.66843	0.31497	512.51		
			Av.	513.80		
Ic	138.140	0.73407	0.32417	668.40	87.39	1.46
		0.73659	0.32953	670.46		
			Av.	669.43		
Id	186.184	0.38370	0.32335	1087.87	127.21	2.76
		0.38490	0.40444	1086.07		
		0.42291	0.34701	1081.49		
		0.59400	0.34961	1086.35		
			Av.	1085.45		
IIa	125.102	0.74065	0.38132	428.56	136.53	0.16
		0.73688	0.35274	428.77		
		0.64212	0.34080	428.88		
			Av.	428.74		
IIb	139.126	0.79644	0.44955	572.23	115.78	1.91
		0.76056	0.48456	569.28		
		0.60563	0.32641	568.68		
		0.65168	0.33505	569.54		
			Av.	569.93		
IIc	153.156	0.72966	0.36090	735.50	118.52	0.72
		0.65792	0.37292	734.12		
		0.76662	0.34216	735.49		
		0.81969	0.38178	734.41		
			Av.	734.88		
IId	201.20	0.70970	0.40355	1147.05	159.53	5.37
		0.40085	0.33132	1157.72		
		0.47111	0.32300	1151.55		
			Av.	1152.11		

The nitric acid correction was found by titration. The calorie equivalent never exceeded 0.25 % of the total heat evolved. The heat of combustion of the bomb process was corrected to 298° K. with each of the reactants and products in its thermodynamic standard state (*4*). The enthalpy of combustion was determined using the formula, $\Delta H = \Delta E + \Delta_\eta RT$. Finally, the enthalpies of formation, ΔH_f, at 298° K., of the triazoles were calculated with the use of data from Rossini *et al.* (*5*). The standard deviation of the heat of combustion in kilocalories per mole is also given in Table II.

Differential Thermal Analysis. Thermograms were obtained on the azido-*s*-triazoles using a Du Pont 900 differential thermal analyzer. The finely divided solids were introduced into a 2-mm. diameter capillary tube to a depth of 3 mm. A Chromel-Alumel thermocouple wire was inserted in the tube so that the junction was maintained in intimate contact with the sample. Fine glass beads were the inert material

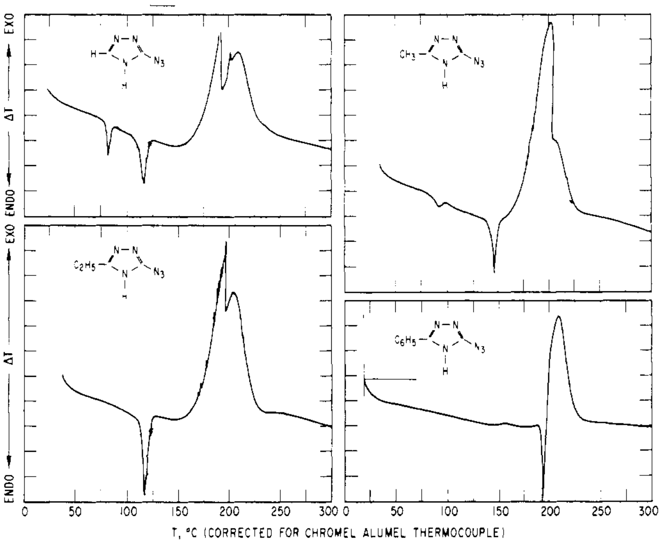


Figure 1. Thermograms of 3-azido-s-triazoles

Size. 2-mm. diameter, 3-mm. depth

Glass beads

Program mode. Heating

Rate. 30° C. per minute

Atmosphere. Air

Scale setting. *T*. 50° C./sq. inch. Δ*T*. 2° C./sq. inch.

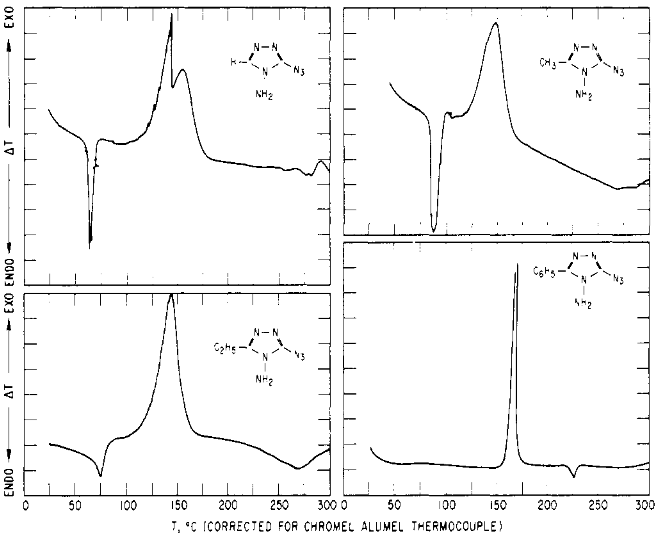


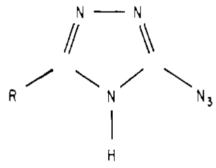
Figure 2. Thermograms of 4-amino-3-azido-s-triazoles
Size. 2-mm. diameter, 3-mm. depth
Glass beads
Program mode. Heating
Rate. 30° C. per minute
Atmosphere. Air
Scale setting. T. 50° C./sq. inch. ΔT. 2° and 5° C./sq. inch

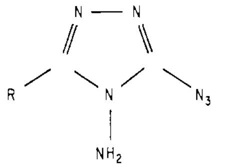
Ia and IIa, R = hydrogen
Ib and IIb, R = methyl
Ic and IIc, R = ethyl
Id and IId, R = phenyl

used in the reference tube. A temperature programmer maintained the rate of heating at 30° C. per minute and the samples were analyzed in an air environment. Different heating rates and using oxygen or nitrogen atmosphere showed no appreciable difference in their thermograms.

RESULTS AND DISCUSSION

Eight triazolyl azides were prepared in which the substituents on the 5-position of 3-azido-s-triazoles, I, and 4-amino-3-azido-s-triazoles, II, were varied from hydrogen, methyl, ethyl, to phenyl. The structures of these compounds are as follows:


I


II

Although the structure for I is written with the hydrogen on the 3-position, other tautomeric forms with the hydrogen on either 1- or 2-nitrogen are also possible. Both I and II are sensitive to heat and light, making purification extremely difficult. In particular, II turns pinkish upon standing and is readily converted to 3-amino-6-substituted-s-tetrazine (*7*) by heating in an inert solvent.

Combustion data for I and II are tabulated in Table II. Considerable difficulties were encountered in achieving clean and complete combustion of the triazoles, despite variation in experimental conditions. Similar difficulties were reported by Williams, McEwan, and Henry (*10*). Since the exact nature of the unburnt residue is not readily ascertained, runs where significant residue (>0.25 weight %) remained were not included.

With the exception of IIb, the heats of combustion appear to be consistent for the two series of triazolyl azides in varying the 5-substituents. The increase in heat of combustion from Ia to Ib is similar to that reported by Williams, McEwan, and Henry for 5-*H* and 5-methyl-*s*-triazole derivatives. Based on these results, it appears that the value for IIb is approximately 10 kcal. per mole low. Neither the use of freshly prepared samples nor numerous attempts at purification using different solvents gave a higher value. In fact, a brown oily film was always obtained as residue in the calorimeter, indicating incomplete combustion. The authors are unable to explain the unique behavior of this particular compound when other similar azidotriazoles gave satisfactory results. The data for IIb, nevertheless, are included in Table II.

Differential thermal analyses were carried out on these azides to determine their thermal stability. Azides of group II all showed characteristic exotherms at about 150° C., whereas azidotriazoles, I, exhibited exotherms at approximately 200° C. The thermograms are shown in Figures 1 and 2. The results show that the lack of amino substituent at the 4- position of the 3-azido-*s*-triazoles imparts approximately 50° C. of greater stability to the triazole ring.

The azidotriazoles investigated in this work exhibit an extremely high heat of formation in comparison to that reported for nitramine and amine nitrate of *s*-triazoles. This high exothermicity is undoubtedly due to the presence of the azido group. In particular, IIa exhibits a value of 109.5 kcal. per 100 grams of material, which is comparable to that of available propellant ingredients. However, of the two series of azides studied, it appears that the 3-azido-*s*-triazoles, despite a somewhat lower heat of formation, offer greater promise in propellant application due to their thermal stability and shock insensitivity.

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