for the Pd(II) chelate, for which the first band appears at 340 m $\mu$ .

The crystal-field approach to the prediction of low-intensity "forbidden" absorption bands of the transition metal complexes, carried out with considerable success by Bjerrum, *et al.*,<sup>13</sup> was not attempted in this investigation, in view of the greater complexity and lower symmetry of the metal chelates of the tetradentate Schiff bases.

In a recent investigation on bisacetylacetone-(13) J. Bjerrum, C. J. Ballhausen and C. K. Jorgensen, Acta Chem. Scand., 8, 1275 (1954), (and later papers). Cu(II) by paramagnetic resonance absorption,<sup>14</sup> it was proved that the metal and ligand were involved in rather strong  $\pi$ -bonds. Bisacetylacetoneethylenediimine-Cu(II), as well as the corresponding Ni(II) chelate, would have similar  $\pi$ bond character, and the high degree of resonance in the chelate rings including the central metal ion would be responsible for the considerable change in the ultraviolet absorption spectra when one goes from the ligands to the metal chelates.

(14) B. R. McGarvey, THIS JOURNAL, 60, 71 (1956).

# THE HEATS OF COMBUSTION OF SUBSTITUTED TRIAZOLES, TETRAZOLES AND RELATED HIGH NITROGEN COMPOUNDS

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The heats of combustion of some 36 substituted triazoles, tetrazoles and related high nitrogen compounds have been determined. The number of moles of nitric acid formed during the combustion process was found to be a function of the square root of the product of the heat of combustion and the number of nitrogen atoms present. Several new tetrazole compounds including the *cis* and *trans* isomers of 1,1'-dimethyl- and 1,1'-diethyl-5,5'-azotetrazole, are described.

The heats of combustion  $(H_{\rm e})$  of a number of tetrazoles were reported by McEwan and Rigg<sup>1</sup> in 1951. Since that time the heats of combustion of a number of additional compounds have been determined. The samples were prepared as part of a study on preparation and properties of high nitrogen compounds and only in a few cases specifically for heat of combustion determinations. For this reason the amount of material available limited the number and size of samples to be run on a given compound.

Some of the triazoles did not burn cleanly or completely. Carbon deposits were found on the bomb wall after combustion; and increasing the oxygen pressure, decreasing the sample size or addition of benzoic acid did not always correct this tendency.

A number of azotetrazoles were prepared in order to have a series of compounds for combustion, which would contain more than one nitrogennitrogen double bond in the molecule per tetrazole ring. 5-Tetrazolylazo-(N)-piperidine met this requirement but like some of the triazole derivatives could not be burned cleanly. Compounds such as 3-(5-tetrazolylazo)-butanone-2, 3-(5-tetrazolylazo)pentanedione-2,4, etc., also were made for this purbut some uncertainty exists, because of pose: tautomerism, as to whether the compounds are present in the azo or hydrazo forms. Oxidation of 1- or 2-alkyl-5-aminotetrazole with sodium hypochlorite furnished the corresponding 5,5'-azotetra-zoles; with the 1,1'-dimethyl- and the 1,1'-diethyl-5,5'-azotetrazole, both the *cis* and the *trans* isomers were ultimately isolated and characterized. With the 2,2'-dialkyl-5,5'-azotetrazoles only one isomer (probably the cis) was recovered.

Smooth combustion of some of these 5,5'-azo-

(1) W. S. McEwan and M. W. Rigg, J. Am. Chem. Soc., 73, 4725 (1951).

tetrazoles derivatives was also very difficult. The compounds would detonate (audible sound on ignition and shattered crucible) and deposit partially burned material on the bomb wall. Another apparent complication was noted: the heat of combustion of *trans-1,1'-dimethyl-5,5'-azotetrazole* seemed to increase with the age of the material (as much as 12 to 15 kcal. per mole in about four months time) although the melting point remained constant. The average heats of combustion for both the cis and the trans forms of 1,1'-dimethyl-5,5'-azotetrazole are given in Table I. Although an energy difference should exist between the cis and trans forms, the large deviations and lack of precision make any difference meaningless. Similar difficulties were encountered with the isomers of 1,1'-diethyl-5,5'-azotetrazole. A total of six samples were burned; of these only one burned cleanly enough to merit calculation. This single value of 1078 kcal. per mole was obtained on the more stable *cis* form.

An original intention in this work was to compute a set of standard bond energies applicable to high nitrogen compounds. Difficulties in obtaining compounds of unambiguous structure, in obtaining heat of sublimation values for all compounds, and the bulk of the data to be presented have caused this portion of the work to be deferred for later publication.

#### Materials

Tetrazole Derivatives.—5-Dimethyl- and 5-diallyl-aminotetrazole were synthesized by the method of Garbrecht and Herbst.<sup>2</sup> The former compound melted at 237–239° dec. after four recrystallizations from water; the latter at 96-97° after five recrystallizations from benzene (calcd. eq. wt., 165.20; found, 165.24).

1-Allyl-5-aminotetrazole (four times recrystallized from ethyl acetate, m.p. 128.5-129.5°), 1-methyl-5-aminotetra-

(2) W. L. Garbrecht and R. M. Herbst, J. Org. Chem., 18, 1003 (1953).

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COMBUSTION DATA									
Compound 5-Aminotetrazole N—NH    >CNH2	Formula CH3N5	Mol. wt. Rigg and	Samp. wt. McEwan	<u>Иннов</u> Изатр. 1	<i>— ∆H</i> ₀	$-\Delta H_{\rm e}({ m av})$ kcal./mole 246.20 ± (	.) ). 56	– <i>∆Ht</i> – 49.67	
$ \begin{array}{c} \overset{\text{I}}{\text{N}} & - \overset{\text{I}}{\text{N}} \\ 1 - \text{Mothyl-5-aminototrazole} \\ \overset{\text{N}}{\text{N}} & - \overset{\text{N}}{\text{N}} - \overset{\text{CH}_3}{\text{CH}_2} \\ & & \\ & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & &$	C2H5N5	99.100 <sup>*</sup>	1.1215 0.9201 1.0258 1.0743	0.213 220 .221 .219	405.14 404.89 405.20 405.42	405.16 ±	.11	-46.2	
2-Methyl-5-aminotetrazole $H_3C-N-N$ N=N N=N	$C_2H_5N_6$	99.100	0.8520 .7134 .5686 .6132 1.0223	. 224 . 229 . 235 . 229 . 224	408.99 410.39 410.52 408.11 408.51	409.30 ±	. 49	-50.40	
5-Methylaminotetrazole N-N-H $\parallel$ N-N N-N	$C_2H_5N_5$	99.100	0.5926 .8878 .7785	.237 .225 .232	$\begin{array}{r} 406.61 \\ 407.12 \\ 408.20 \end{array}$	407.31 ±	. 47	-48.41	
1-Methyl-5-methylaminotetrazole $N-N-CH_3$ $\parallel$ N-N N-N	C <sub>3</sub> H <sub>7</sub> N <sub>5</sub>	113.126	.9722 1.0489 1.0614	. 267 . 259 . 262	569.45 568.68 569.13	569.09 ±	.70	-47.82	
5-Dimethylaminotetrazole N - N - H M - N - H M - N - N	C₃H7N₅	113.126	0.7821 .6945	. 275 . 324	564.41 565.49	564.95 ±	. 54	43.68	
1,3-Dimethyl-5-iminotetrazole nitrate $N \rightarrow N \rightarrow CH_3$ $\downarrow \pm C = NH \cdot HNO_3$ $N \rightarrow N$ $\downarrow CH_3$	C8H8N6O3	176.142	. 5447 . 5097	.584 .693	554.45 553.84	554.15 ±	.30	+1.28	
$\begin{array}{c c} 1-Allyl-5-aminotetrazole\\ N-N-CH_2CH=CH_2\\ \\ \\ \\ \\ \\ \\ \\ N-N \end{array}$	C₄H7N₽	125.136	.7131 .6327 .7356 .5859 1.1870 0.9929	.282 .276 .271 .274 .249 .273	677.83 678.95 678.39 677.90 679.26 679.22	$678.75 \pm$	.22	- 63.43	
2-Allyl-5-aminotetrazole CH <sub>2</sub> =CHCH <sub>2</sub> -N-N N=N	C₄H7N₅	125.136	. 4208 . 5966	. 275 . 273	$683.12 \\ 682.74$	682.93 ±	. 19	-67.61	
$\begin{array}{c c} 1-Allyl-5-allylaminotetrazole\\ N-N-CH_2CH=CH_2\\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ $	$C_7H_{11}N_8$	165.198	. 9346 . 7959	.342 .351	1117.33 1118.29	1117.81 ±	. 52	83.70	
5-Diallylaminotetrazole N-N-H $\parallel$ $>$ CN(CH <sub>2</sub> CH=CH <sub>2</sub> ) <sub>2</sub> N-N	$C_7H_{11}N_5$	165.198	. 8066 . 7650 . 5259 . 4986	$.305 \\ .344 \\ .356 \\ .352$	$\begin{array}{c} 1118.65\\ 1118.32\\ 1117.89\\ 1117.26\end{array}$	1118.03 ±	.54	83 . 92	
5-Phenylaminotetrazole N - N - H $\parallel$ CNHC <sub>6</sub> H <sub>6</sub> N - N	C7H7N₅	161.166	.3246 .3564	.282 .315	970.40 970.35	970.37 ±	.02	-72.89	
1-Phenyl-5-aminotetrazole $N-C_6H_5$ $CNH_2$ N-N	$C_7H_7N_8$	161.166	. 5688 . 4510 . 4612	.297 .312 .318	971.34 971.42 972.57	971.78 ±	. 40	74.30	

# TABLE I

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# HEATS OF COMBUSTION OF SUBSTITUTED TRIAZOLES

	TABL	EI (Cont	linued)				
$\begin{array}{c} Compound \\ trans-1,1'-Dimethyl-5,5'-azotetrazole \\ N-N-CH_8 H_3C-N-N \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\$	Formula C4H6N10	Mol. wt. 194.168	$\begin{array}{c} s_{amp.} \\ wt. \\ 0.6502^a \\ .5892 \\ .4709 \\ .3814 \\ .8643^a \\ .6685 \\ .6285 \\ .5026^a \\ .6315 \end{array}$	$\frac{N_{\rm HNO_3}}{N_{\rm samp.}}$ 0.662 .525 .545 .548 .846 .572 .456 .620 .470	$-\Delta H_0$ 767.88 770.76 776.73 7765.01 765.01 763.86 761.32 770.34 782.13	$\begin{array}{l} -\Delta H_{0}(\mathbf{sv.}) \\ \text{kcal./mole} \\ 770.49 \pm 2.42 \end{array}$	- Δ <i>Ht</i> - 189.33
$\begin{array}{c} \mathfrak{sis-1,1'-Dimethyl-5,5'-azotetrazole} \\ \mathbb{N} \longrightarrow \mathbb{C} + \mathbb{N}  \mathbb{C} - \mathbb{N} = \mathbb{N} - \mathbb{C}  \mathbb{N}  \mathbb{N} \end{array}$	C4H6N10	194. <b>168</b> i	.6184 .5884	.445 .397	769.69 769.87	769.78 ± 0.09	-188.62
2,2'-Dimethyl-5,5'-azotetrazole H <sub>s</sub> C-N-N N-CH, N=N N=N	C4H6N10	194.168	, 4934 , 4825	.584 .693	762.04 761.09	761.51 ± .53	180.35
$\begin{array}{c c} 2,2'-\text{Diethyl-5,5'-azotetrazole} \\ H_5C_2-N-N & N-N-C_2H \\ & & \\ & \\ & & \\ & \\ & & \\ & \\ & & \\ & & \\ & & \\ & \\ & & \\$	C6H10N10	222.2Ż	.3968 .3106 .4673	.500 .523 .529	1061.39 1062.65 1063.79	$1062.52 \pm .70$	-156.62
3-(5-Tetrazolylazo)-butanone-2 N-N-H N-N N-N N-N-H N-N-H N-N-H N-N-H N-N-H N-N-H	C6H2N6O	168.162	. 4295 . 4691 . 3931	.335 .340 .335	783.42 783.49 783.70	783.53 ± .08	-40.00
3-(5-Tetrazolylazo)-pentanedione-2,4 N-N-H N-N H N-N H N-N H N-N $CNHN=C(COCH_3)COCH_3$	C6H8N6O2	196.172	.6542 .6062 <sup>b</sup> .8126 .6153	.269 .352 .256 .303	837.84 841.50 840.22 844.29	840.96 ± 1.34	-3.38
$N - N$ Benzal 5-hydrazinotetrazole $N - N - H$ $  \qquad > CN = NCH_2C_8H_5$ $N - N +$ $  \qquad > CN + H$ $  \qquad > CN + H$ $  \qquad > CN + H$ $  \qquad > CHC_8H_6$	C <sub>8</sub> H <sub>8</sub> N <sub>8</sub>	188.192	.9505 .7645 .8970	.317 .344 .312	1130.99 1130.86 1131.42	$1131.06 \pm 0.17$	-105.41
1-Phenyl-5-methyltetrazole <sup><math>\circ</math></sup> N-N-C <sub>6</sub> H <sub>5</sub> $\searrow$ CCH <sub>3</sub> N-N	C <sub>8</sub> H <sub>8</sub> N <sub>4</sub>	160.176	.7660 .7179	.299 .329	1095.07 1094.60	1094.84 ± .24	-69.15
$\begin{array}{c c} 1-Methyl-5-phenyltetrazole\\ N-N-CH_{s}\\ & \searrow CC_{6}H_{5}\\ N-N \end{array}$	C <sub>8</sub> H <sub>8</sub> N <sub>4</sub>	160.176	.4593 .4462	.323 .324	1095.38 1095.68	$1095.53 \pm .15$	-69.84
5-Methoxytetrazole N-N-H N-N N-N	C <sub>2</sub> H <sub>4</sub> N <sub>4</sub> O	100.084	.4471 .3843 .4611	.190 .198 .190	$341.50 \\ 341.33 \\ 340.93$	$341.25 \pm .17$	-16.51
5-Hydroxytetrazole N-N-H COH N-N	OH₂N₄O	86.058	$.6396 \\ .7436 \\ .6181 \\ .5520 \\ 1.4491$	.113 .108 .109 .102 .106	$163.49 \\ 163.54 \\ 164.32 \\ 163.47 \\ 164.56$	163.88 ± .23	-1.50

	TABLE I (Continued)			Nuvo				
Compound	Formula	Mol. wt.	Samp. wt.	Naamp.	ΔHe	$-\Delta H_{e}(av.)$ kcal./mole	$-\Delta H_{f}$	
1,4-Dimethyl-5-tetrazolone NN-CH,	C <sub>8</sub> H <sub>6</sub> N <sub>4</sub> O	114.100	0.6325 1.0038	0.213 .212	$\begin{array}{r} 479.92\\ 480.93 \end{array}$	$480.42 \pm .50$	-6.69	
CH <sub>3</sub> 5-Cyanotetrazole NNH	C <sub>2</sub> HN <sub>6</sub>	95. <b>068</b>	0.4745 5058 <sup>b</sup>	.145	318.47 318.23	$318.35 \pm .12$	-96.09	
			10000		010.20			
1-(5-Tetrazolyl)-4-guanyltetrazene hydrate	$C_2H_8N_{10}O$	188.164	. <b>6282</b> . 7957	. 455 . 409	506.66 507.50	$506.58 \pm .08$	-45.20	
$\begin{bmatrix} H_2 NC(NH)NHNHN=N-C \\ N-N \end{bmatrix} H_2 M_2 M_2 M_2 M_2 M_2 M_2 M_2 M_2 M_2 M$	0							
1,2-Di-(5-tetrazolyl)-ethane N-N-H $H-N-NCCH_{2}CH_{2}C$	C4H6N8	166.152	.4227 .4157	.393 .348	687.21 687.50	687.36 ± .15	106 . 20	
Ilydrazodicarbamide H2NCONHNHCONH2	C <sub>2</sub> H <sub>6</sub> N <sub>4</sub> O <sub>2</sub>	118.100	. 6852 <sup>b</sup> . 3288 <sup>b</sup>	$.152 \\ .178$	$273.97 \\ 273.53$	273.87 ± .14	+119.19	
A 14 1 19	<b>G II</b> N O		.9890 <sup>6</sup> .7416	. 136 . 153	274.19 273.79		1 00 01	
Azodicarbamide H <sub>2</sub> NCON=NCONH <sub>2</sub>	C <sub>3</sub> H <sub>4</sub> N <sub>4</sub> O <sub>3</sub>	116.084	.9156 .5936	.122	253.07 256.58	$254.83 \pm .25$	+69.91	
Acetamidoguanidine nitrate CH <sub>3</sub> CONHNHC(NH)NH <sub>2</sub> ·HNO <sub>3</sub>	C <sub>8</sub> H <sub>8</sub> N <sub>5</sub> O <sub>4</sub>	179.142	.8407 .9197°	.215 .240	471.09 472.00	$471.55 \pm .55$	+118.04	
1-Acetamido-2-nitroguanidine CH <sub>3</sub> CONHNHC(NH <sub>2</sub> )NNO <sub>2</sub>	$C_3H_7N_8O_8$	161.126	1.2724 1.2593	. 182 . 162	474.69 475.28	474.99 ± .70	+46.28	
1-Formamido-2-nitroguanidine HCONHNHC(NH2)NNO2	$C_2H_5N_5O_3$	147.100	0.8797 .7592	. 167 . 173	323.75 323.85	$323.80 \pm .05$	+35.10	
3-Amino-1,2,4-triazole HN-N	$C_2H_4N_4$	84.084	$1.0300 \\ 1.0962 \\ 1.1441$	. 165 . 159 159	$343.72 \\ 342.11 \\ 343.48$	343.10 ± .47	-18.36	
C = N			1,1331	. 100	010.10			
3-Amino-1,2,4-triazole nitrate	$C_2H_5N_5O_3$	147.100	$0.5470 \\ 1.0524 \\ 1.0088$	.172 .177 .177	320.01 315.95	$318.01 \pm 1.17$	+140.89	
C = N			1.0000	.170	318.00			
3-Amino-5-methyl-1,2,4-triazole nitrate H-N-N	C <sub>3</sub> H <sub>7</sub> N <sub>5</sub> O <sub>3</sub>	161.126	0.5621 .5351	.228 .228	467.09 466.27	$466.68 \pm 0.41$	+54.59	
$H_{3}C-C=N$								
3-Nitramino-5-methyl-1,2,4-triazole HNN	$C_8H_5N_5O_2$	143.100	.6499 .8756 <sup>6</sup>	.222 .256	$\begin{array}{r} 465.06 \\ 465.50 \end{array}$	$465.67 \pm 0.19$	-12.72	
H-C-C=N			1.1354 0.8032	.209 .218	$\begin{array}{r} 465.80\\ 465.51 \end{array}$			
3-Nitramino-1,2,4-triazole	$C_2H_8N_bO_2$	129.084	.7148 .4819	. 190	$314.91 \\ 318.47$	$317.45 \pm 1.00$	-26.87	
CNHNO2			. 4092 . 8356	. 193 . 196	$\begin{array}{r} 319.48\\ 316.94 \end{array}$			
nC==N Benzal 3-hydrazino-5-methyl-1,2,4-triazole	$C_{10}H_{11}N_{5}$	201,228	. 5849	.356	1378.22	$1377.87 \pm 0.25$	-61.60	
H-N-N CNHN=CHC <sub>6</sub> H <sub>5</sub>			. 5644 . 4540	.397 .360	$1377.38 \\ 1378.01$			
$H_aC - C = N$								

<sup>a</sup> Sample detonated. <sup>b</sup> Benzoic acid added. <sup>c</sup> Rigg (ref. 1) reported 1096.26  $\pm$  0.07 kcal./mole for  $-\Delta H_{\bullet}$ .

zole (three times recrystallized from water, m.p.  $226.5-227.5^{\circ}$ ), 5-methylaminotetrazole, 1-phenyl-5-aminotetrazole, 5-anilinotetrazole (four times recrystallized from

33% aqueous ethanol, m.p.  $209{-}210^\circ)$  and 1-methyl-5-methylaminotetrazole (two times recrystallized from absolute ethanol, m.p.  $173.5{-}174.5^\circ)$  were prepared from

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appropriate thioureas by previously reported procedures.<sup>4</sup> The samples of 2-allyl- and 2-methyl-5-aminotetrazole<sup>4</sup> melted at 67-68° and 105.5-106.5°, respectively, after several recrystallizations. 1,3-Dimethyl-5-iminotetrazole nitrate<sup>8</sup> was recrystallized three times from absolute eth-anol, m.p. 152.5-153.5°. Benzal 5-hydrazinotetrazole<sup>9</sup> was recrystallized several times from acetic acid: m.p. 235-236° dec.

1-Ally1-5-allylaminotetrazole was made in 82% yield from 1,3-diallylthiourea by the procedure outlined in ref. 3. After three recrystallizations from diethyl ether (1 ml. per g.) the compound melted at 48.5-49.5°.

Anal. Calcd. for C<sub>7</sub>H<sub>11</sub>N<sub>8</sub>: C, 50.89; H, 6.71; N, 42.40. Found: C, 51.09; H, 6.69; N, 41.89, 42.62.

1.2-Diallyl-3-aminoguanidine hydroiodide. a.n intermediate in the above preparation, melted at 126-127°. after recrystallization from absolute ethanol.

Anal. Caled. for  $C_7H_{16}N_4I$ : C, 29.80; 5.36; I, 44.98. Found: C, 29.77; H, 5.35; I, 44.86.

1,2-Di-(5-tetrazolyl)-ethane.-A procedure described by Mihina and Herbst<sup>7</sup> was employed. A solution consisting of 8.81 g. (0.11 mole) of succinonitrile, 16.5 g. (0.23 mole) of sodium azide, 16.8 g. (0.28 mole) of acetic acid and 35 ml. of isopropyl alcohol was heated in a sealed ampule at 150° for 52 hours. The contents of the cooled ampule were dissolved in aqueous ethanol, filtered and evaporated to dryness under reduced pressure. The residue was redis-solved in water, treated with 30 ml. of concentrated hydrochloric acid, and re-evaporated to dryness under reduced pressure. This residue was then extracted with two 100-ml. portions of 95% ethanol, and the extracts evaporated. This crude product was dissolved in 200 ml. of hot acctonitrile, filtered, cooled, and the compound removed by filtra-tion; 8.6 g. (51.8%); m.p. 218-220°. One recrystalliza-tion from 400 ml. of acetonitrile plus 150 ml. of absolute ethanol raised the m.p. to 233-234° dec. Two recrystal-lizations from isopropyl alcohol finally yielded 2.0 g. of compound decomposing at 245-247°.

Anal. Calcd. for C<sub>4</sub>H<sub>6</sub>N<sub>8</sub>: C, 28.91; H, 3.64; eq. wt., 83.08. Found: C, 28.87; H, 3.74; eq. wt., 85.39.

Recrystallized samples of 5-cyano, 5-hydroxy- and 5-methoxytetrazole, generously supplied by K. Hattori and E. Lieber, Illinois Institute of Technology, were used as received. The sample of 1,4-dimethyl-5-tetrazolone, also supplied by Hattori and Lieber, was purified by two low pressure sublimations. The purified 1-(5-tetrazolyl)-4-guanyltetrazene hydrate<sup>8</sup> was furnished by S. Patinkin. 1-Phenyl-5-methyltetrazole made by the method of

1-Phenyl-5-methyltetrazole, made by 5.1 kulturi Dimroth and DeMontmollin, was recrystallized twice from ethyl acetate, m.p. 97–98°. The isomeric 1-methyl-5-phenyltetrazole<sup>10</sup> was recrystallized three times from water,

m.p. 104-105°. The 2,2'-diethyl-5,5'-azotetrazole.—2-Ethyl-5-aminotet-razole (28.8 g., 0.255 mole) was dissolved in 200 ml. of water and treated all at once with 380 ml. of 5% sodium hypochlorite solution (0.255 mole). The solution was stirred hypochiorite solution (0.255 mole). The solution was stirred for several hours at room temperature, then allowed to stand overnight at 5°. The product was removed by fil-tration, washed with a small volume of cold water, and recrystallized from 25% aqueous ethanol. The yield of once recrystallized compound was 17.8 g. (63%); orange needles, m.p. 110-111°;  $\lambda_{max} 293 \text{ mm} (25\% C_2H_3)(H), \epsilon 14,370.$ 

Anal. Calcd. for  $C_6H_{10}N_{10}$ : C, 32.43; H, 4.54; N, 63.04. Found: C, 32.6; H, 4.56; N, 62.33.

1,1'-Diethyl-5,5'-azotetrazole was prepared in 29% yield from 1-ethyl-5-aminotetrazole<sup>3</sup> by the same procedure as above. After one recrystallization from 25% aqueous eth-

(3) W. G. Finnegan, R. A. Henry and E. Lieber, J. Org. Chem. 18, 779 (1953).

(4) R. A. Henry and W. G. Finnegan, J. Am. Chem. Soc., 76, 923 (1954).

(5) R. A. Henry, W. G. Finnegan and E. Lieber, ibid., 76, 2894 (1954).

(6) J. Thiele and J. T. Marais, Ann., 273, 144 (1893).

(7) J. S. Mihina and R. M. Herbst, J. Org. Chem., 15, 1082 (1950).

(8) S. H. Patinkin, J. P. Horwitz and E. Lieber, J. Am. Chem. Soc., 77, 562 (1955).

(9) O. Dimroth and G. DeMontmollin, Ber., 43, 2907 (1910)

(10) E. K. Harvill, R. M. Herbst, E. C. Schreiner and C. W. Roberts, J. Org. Chem., 15, 662 (1950).

anol, the rosettes of very fine orange needles decomposed at 118-119°

Anal. Calcd. for CeH10N10; C. 32.43; H. 4.54; Found: 32.46: H. 4.56.

This product was ultimately separated into two isomeric compounds by repeated fractional crystallizations from 25% ethanol: (1) a less soluble fraction; small bright yel-low needles, m.p. 129-130° dec.;  $\lambda_{max}$  375 mµ (25% C<sub>1</sub>H<sub>s</sub>-OH), e 9,230.

Anal. Calcd. for  $C_{6}H_{10}N_{10}$ : C, 32.43; H, 4.54; N, 63.04. Found: C, 32.84; H, 4.59; N, 62.29.

(2) A more soluble fraction; large, flat orange needles, m.p. 168-169° dec.;  $\lambda_{max}$  303-304 mµ (25% C<sub>2</sub>H<sub>5</sub>OH), e 13,480.

Anal. Calcd. for  $C_6H_{10}N_{10}$ : C, 32.43; H 63.04. Found: C, 32.22; H, 4.62; N, 63.16. H. 4.54: N.

The low melting isomer is considered to be the trans compound since its ultraviolet absorption spectrum is almost identical with that for the trans 1.1'-dimethyl-5.5'azotetrazole (see below).

2,2'-Dimethyl-5,5'-azotetrazole was made in a similar manner from 2-methyl-5-aminotetrazole; orange needles after recrystallization from water; m.p. 170–171° dec.

Anal. Calcd. for  $C_{4}H_{6}N_{10}$ : C, 24.74; H, 3.12; N, 72.14. Found: C, 24.48, 24.88; H, 2.79, 3.27; N, 72.48.

1.1'-Dimethyl-5,5'-azotetrazole was obtained as bright yellow needles, decomposing at 149-150°, when the fol-lowing procedure was employed. Recrystallized 1-methyl-5-aminotetrazole (10 g., 0.10 mole) was slurried with 100 ml. of water. Aqueous sodium hypochlorite solution (150 ml. of 5%, 0.1 mole) was added with good agitation during 2.5 hours; the stirring was continued for one hour. The solution, after dilution with 50 ml. of water, was heated to boiling to complete the reaction and to dissolve the pre-cipitated azo compound. After the solution had been filtered and cooled to room temperature, the compound was removed and dried. The yield was 5.6 g. (58%). Recrys-tallization from water did not change the decomposition temperature. Single crystal X-ray patterns indicated that this compound had a center of symmetry<sup>11</sup>; primarily on this basis the *trans* configuration is assigned. An aqueous solution of this form showed a maximum absorption in the ultraviolet spectrum at 372 mµ; e 9,220.

Anal. Calcd. for C4H6N10: C, 24.74; H, 3.12; N, 72.14. Found: C, 24.72; H, 3.19; N, 72.78, 72.93.

The trans compound also exists in a polymorphic form; short, yellow prisms, m.p. 162-163° dec.;  $\lambda_{max}$  372 mµ (H<sub>2</sub>O),  $\epsilon$  9190. Admixture with the low melting trans form did not depress the melting point.

Anal. Calcd for C<sub>4</sub>H<sub>6</sub>N<sub>10</sub>: C, 24.74; H, 3.12; N, 72.14. Found: C, 24.73; H, 2.81; N, 72.50.

Attempts to convert this yellow form to an azoxy com-pound by heating with glacial acetic acid-30% hydrogen peroxide gave a product which melted at 183-184° dec., after recrystallization from water as orange, flat needles. Admixture with the starting compound lowered the melting point to 120-130°. However, the analyses did not indicate an azoxy compound but rather an azo compound. This orange form is more soluble in water than the yellow form and the maximum absorption in the ultraviolet spectrum of an aqueous solution occurs at  $301-302 \text{ m}\mu$ ,  $\epsilon 12,970$ . The *cis*-configuration is assigned tentatively. The *trans* form can also be converted quantitatively (based on the com-plete disappearance of the absorption peak at 372 m $\mu$  and the appearance of the peak at 302 m $\mu$ ) to the *cis* form by allowing an aqueous solution of the former to stand for several days in sunlight.

Anal. Calcd. for  $C_4H_6N_{10}$ : C, 24.74; H, 3.12; N, 72.14. Found: C, 24.66, H, 3.17; N, 71.16.

Stollé, et al.,12 reported 182° dec. for the melting point of

1,1'-dimethyl-5,5'-azotetrazole. 3-(5-Tetrazolylazo)-pentanedione-2,4<sup>13</sup> was recrystallized twice from 50% aqueous ethanol and once from ethyl ace-tate; m.p. 163-164° dec.

3-(5-Tetrazolylazo)-butanone-218 after two recrystalliza-

(11) Private communication from J. H. Bryden of this Laboratory. (12) R. Stollé, K. Ehrmann, D. Rieder, H. Willie, H. Winter and F. Henke-Stark, J. prakt. Chem., 134, 282 (1932).

(13) Unpublished work of R. A. Henry and L. D. Dyer.

tions from ethyl acetate-ethanol (2:1) melted at 175.5°. 5-Tetrazolylazo-(N)-piperidine.—5-Aminotetrazole mono-

by drate (4.85 g.) was diazotized according to the procedure of Bülow<sup>14</sup>; after 20 minutes 4 g. of piperidine in 15 ml. of water was added all at once. The resulting solution ( $pH \sim$ 4) was stirring for 25 minutes at 0-5°, then allowed to stand overnight at 0°. A white solid began to separate after five minutes and gradually increased in amount with the stand-ing. The solid was removed by filtration and washed with ing. The solid was removed by filtration and wasned with two 15-ml. portions of cold water. The yield of air-dried product (m.p. 110-115°) was 6.6 g. (77.7%). Two re-crystallizations in the following manner raised the melting point to 126-127° (vigorous decomposition): 150 ml. of water was heated to 65°, the compound was added with rapid stirring to assist the dissolution, and the solution was filtered into a flask cooled in an ice-bath. If the water is the point or too much time is taken to affect the recrystal too hot or too much time is taken to effect the recrystallization, considerable decomposition with gassing occurs.

Anal. Calcd. for  $C_6H_{11}N_7$ : C, 39.77; H, 6.12; N, 54.11; eq. wt., 181.22. Found: C, 40.09; H, 6.03; N, 53.82; eq. wt., 182.9, 181.8.

Guanidine and Triazole Derivatives.—Hydrazodicarb-amide, made by the method of Leboucq,<sup>15</sup> was recrystallized twice from large volumes of water; m.p. 248°. Azo-dicarbamide<sup>16</sup> was made by oxidizing the hydrazo compound with potassium dichromate in sulfuric acid solution; recrystallization from water yielded small orange prismatic needles decomposing between 225-230° (depends on rate of heating).

1-Acetamido- and 1-formamido-2-nitroguanidine<sup>17</sup> after three recrystallizations from water decomposed at 195° and 190-191°, respectively. 3-Nitroamino-5-methyl-1,2,4-tri azole<sup>17</sup> and 3-nitramino-1,2,4-triazole<sup>17</sup> prepared from the preceding amides, were also recrystallized three times from water; m.p. 206-207° dec. and 221-222° dec., respectively. Formamidoguanidine nitrate was recrystallized three times from 95% ethanol; m.p. 144-145° (reported<sup>18</sup> 143°); whereas the homologous acetamido compound was recrystal-lized twice from absolute ethanol; m.p. 145.5-146.5° (re-ported<sup>19</sup> 142-143° (dec.)). 3-Amino-5-methyl-1,2,4-triazole was purified as follows.

The crude compound was dissolved in absolute ethanol, decolorized with charcoal, filtered, cooled to  $0^{\circ}$  and treated with two volumes of diethyl ether. After several days at with two volumes of diethyl ether. After several days at 0°, the crystalline material was removed and recrystallized twice from dioxane and finally from ethyl acetate. The resulting fine white needles melted at  $151-152^\circ$ ; reported<sup>19</sup> 148°. The corresponding nitrate was recrystallized twice from absolute ethanol to give a product melting at 176-177° (reported<sup>19</sup> 171°). 3-Amino-1,2,4-triazole from Fairmount Chemical Co., often decolorization with charceal in ethanol. was recrystal-

3-Amino-1,2,4-triazole from Fairmount Chemical Co., after decolorization with charcoal in ethanol, was recrystal-lized three times from dioxane; m.p. 156-157°, reported<sup>18</sup> 159°. The nitrate was recrystallized three times from 95% ethanol; m.p. 180.5-181.5°, reported<sup>18</sup> 174° dec. Benzal 3-hydrazino-5-methyl-1,2,4-triazole<sup>20</sup> was re-crystallized from 80% ethanol; m.p. 266°; reported by Thiele and Manchot,<sup>18</sup> 263°.

#### **Experimental Details**

An isothermal precision combustion calorimeter of local construction was used, calibrated with 1-g. samples of Bureau of Standards benzoic acid 39 g. Nineteen calibrations were made during the period in which these samples were run. The heat capacity of the calorimeter and the standard deviation was  $2274.98 \pm 0.35$  cal./°. Other experimental details may be summarized as follows:

a. The calorimeter is completely surrounded by a constant temperature bath which is con-trolled to  $\pm 0.002^{\circ}$ .

(14) C. Bulow, Ber., 42, 4429 (1909).

- (16) J. Thiele, Ann., 271, 127 (1892).
- (17) R. A. Henry, J. Am. Chem. Soc., 72, 5343 (1950).
   (18) J. Thiele and W. Manchot, Ann., 303, 33 (1898).
- (19) J. Thiele and K. Heidenreich, Ber., 26, 2598 (1893).

(20) E. Lieber, S. Schiff, R. A. Henry and W. G. Finnegan, J. Org. Chem., 18, 218 (1952).

b. The same weighed quantity of water  $(\pm 0.1 \text{ g})$ is used in the calorimeter in each determination.

c. Temperature measurements were made with a platinum resistance thermometer and a Leeds and Northrup G-2 Mueller bridge to  $\pm 0.0003^{\circ}$ .

d. A 360-ml. Parr double valve oxygen bomb was used. The electrodes of the bomb were modified to make more reliable and reproducible contacts with the fuse wire. The bomb was flushed twice with 25 atm. of oxygen and then filled to 30-31 atm. with oxygen.

e. The ignition system consisted of 90 v. d.c. through 4 to 6 cm. of 0.004 mil platinum wire which carried 0.0012 to 0.0024 g. of fuse paper.

f. One ml. of water was placed in the bomb before ignition.

Samples were in the form of 1/2 inch diameter pellets.

h. A very thin walled platinum crucible weighting 2 to 3 g. was used.

i. Provision was made for either heating or cooling the calorimeter so that adjustment of the calorimeter temperature at time of ignition with respect to bath temperature could be made easily.

#### **Corrections Applied**

Heat transfer between the calorimeter and the constant-temperature bath is determined for each experiment by measuring the rate of temperature change before igniting the sample and after the reaction is complete. The time and resistance are recorded on a Gaertner four-channel chronograph. One channel records the time in seconds. The next channel records a code corresponding to a recorded thermometer resistance by means of a key switch. The third channel records the time at which the sample was fired. By following the temperature-time curve after firing and obtaining a second constant rate after the completion of the reaction the thermal-leakage coefficient and the heat of stirring are obtained by the solution of two equations of the form

#### $\mathrm{d}T/\mathrm{d}t = (Q \times K) + W$

where dT/dt is the change of temperature with respect to time in the calorimeter; Q the thermal head, is the difference between the bath temperature and the calorimeter temperature; K is the thermal-leakage coefficient and W is the rise in temperature produced through stirring.

The thermal-leakage coefficient for the calorimeter was approximately  $4.6 \times 10^{-5}$  degree/sec. and the correction to be applied was determined by graphical integration of the resistance vs. time curve. The temperature rise from stirring W was approximately  $1 \times 10^{-6}$  degree/sec. The average time from ignition to the final rate period was 500 seconds. A 10% deviation in the K value obtained was considered sufficient reason for disqualifying the result obtained on that particular determination.

Very small strips of ashless filter paper were threaded on the ignition wire as an igniter for the samples. The heat of combustion of the paper was found to be  $4032 \pm 2$  cal./g. on 6 determinations. The energy to the ignition wire was measured by a special watt meter and varied from 0.1 to 0.3 cal.

<sup>(15)</sup> J. Leboucq, J. Pharm. Chem., 5, 531 (1927).

A correction for unburnt carbon was rarely used as there is always some uncertainty as to whether the unburnt residue is carbon, unburnt sample or some intermediate product. After the heat of combustion measurements were made, the crucible was removed from the bomb, dried and weighed. The crucible was then heated to red heat, cooled and weighed again. A loss in weight of 0.0002 g. or less was neglected. A loss in weight of 0.0003 to 0.0009 g., when visual inspection showed a thin black film, was treated as carbon and the heat of combustion correction of 7830 cal./ g. was made. If a loss in weight of 0.0010 g. or

more occurred the result was discarded. The minimum and maximum amounts of water present in the bomb after completion of the reaction were calculated for the type of samples burnt in order to determine the dilution of the HNO<sub>3</sub> formed. The molar ratio of HNO<sub>3</sub> to H<sub>2</sub>O varied from 1/24 to 1/40 from which the heat of formation of HNO<sub>3(aq)</sub> from H<sub>2</sub>O, N<sub>2</sub> and O<sub>2</sub> was computed as 15.07 kcal./mole. The number of moles of HNO<sub>3</sub> formed was determined by thoroughly washing the interior walls of the bomb after each combustion and titrating the wash water to a phenolphthalein end-point with 0.1 N NaOH solution.

The heat of solution of  $CO_2$  was taken as 4050 cal./mole and the Washburn<sup>21</sup> figure of 0.004 was taken as the amount of  $CO_2$  going into solution. The heat of combustion was corrected to 25° and 1 atm. pressure by use of the standard Washburn corrections. The heats of formation ( $H_f$ ) of  $CO_2$  and  $H_2O(1)$  were 94.052 and 68.317 kcal./mole, respectively. The results are given in Table I. The standard deviation of the heat of combustion in kcal./mole also is listed.

Nitric Acid Corrections.—Inspection of the accumulated results of the nitric acid determination of these combustions leads one to the conclusion that for cases where a nitric acid determination has not been made a correction can be estimated. The number of moles of nitric acid formed  $(N_{\rm HNOs})$ by the combustion of  $N_{\rm s}$  moles of  $C_{\rm s}H_{\rm b}O_{\rm c}N_{\rm d}$  may

(21) E. W. Washburn, J. Research Natl. Bur. of Standards, 10, 525 (1933).

be calculated by use of the equation

 $N_{\rm HNO_8} = 0.0045 (H_{\circ} \times d)^{1/2} \times N_{\circ}$ 

where the heat of combustion  $(H_c)$  is measured in kcal./mole and d is the number of gram-atoms of nitrogen per formula weight. This equation represents the best straight line through 100 experimental points of a log-log plot. The average deviation of the experimental data from this equation, when converted to the per cent. error produced in the nitric acid correction, was 0.05%.

Three definite exceptions were noted in which the experimentally determined number of moles of nitric acid was significantly higher than the calculated value: (1) when the sample detonated, (2) when the sample was burned with an auxiliary material, and (3) when the sample was in the form of a hydrate (only one hydrate was burned so it is not definitely known whether this is a general exception or not). Only those samples which were definitely known to have detonated are marked. In material of the type burned it is possible that on numerous occasions a low order detonation occurred and there was no visible evidence when the bomb was opened after combustion.

It is felt that the nitric acid correction for combustion experiments of other laboratories will follow the general form of this equation; however, the constant may be a function of specific combustion apparatus employed. Sufficient data from other laboratories are not available to check this point.

The heats of combustion given in this paper have been corrected using the experimentally determined amount of nitric acid. The maximum deviation between the experimental correction and the calculated correction was 12 cal. This equation makes it possible to compute a nitric acid correction when none has been made and to adjust heat of combustion values for varying heats of formation of HNO<sub>3</sub> when sufficient experimental data are not available.

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### ADSORPTION MEASUREMENTS AT VERY LOW PRESSURES. II

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Initial rates of adsorption are measured for CO, CO<sub>2</sub> and N<sub>2</sub> on films prepared by evaporation from the metals Ba, Sr, La, Ti, Zr, Nb, Ta, Cr, Mo, W, Mn, Fe and Ni. While all metals absorb CO at a high rate of more than 2500 cm.<sup>3</sup>/sec. cm.<sup>3</sup>, these metals behave in different ways when adsorbing N<sub>2</sub>. Two groups can be distinguished, one of which, consisting of metals in the center of the periodic table, has a high rate for N<sub>2</sub>, while the other one, consisting of metals located on the sides of the table, has a rate for N<sub>2</sub> which is less than 1 cm.<sup>3</sup>/sec. cm.<sup>2</sup>. The quantities adsorbed are about twice as large for carbon monoxide as for nitrogen. Both these quantities increase considerably if the temperature is raised above a critical value which ranges from 150 to 200° for Ba-CO and Ti-CO. This increase is believed to be due to the onset of surface migration. On titanium and tungsten, nitrogen may be adsorbed subsequent to carbon monoxide while the reverse procedure is not possible.

1. Experimental Procedure.—The method described in a recent publication<sup>1</sup> and illustrated in Fig. 1 has been improved further and measurements have been extended to

a number of transition metals. Experimental improvements

(1) S. Wagener, This JOURNAL, 60, 567 (1956).