ml. of ethyl alcohol gave a yellow precipitate which started to turn orange rapidly. This transformation was completed by heating the mixture four hours on a steam-cone. The washed and dried product weighed 1.2 g. *Anal.* Found: Au, 40.7, 40.75; C, 29.59; H, 1.76; N, 5.65; Cl, 22.18. Calcd. for $AuCl_3C_{12}H_8N_2$: Au, 40.77; C, 29.79; H, 1.67; N, 5.79; Cl, 22.00. The addition of ten drops of concentrated HNO_3 to a solution of 0.20 g. of $[AuCl_2(phen)]Cl$ in 35 ml. of water gave 0.19 g. of a yellow precipitate. *Anal.* Found: Au, 38.7, 38.42; C, 28.64; H, 2.19; Cl, 13.64. Calcd. for $AuCl_2C_{12}H_8N_3O_3$: Au, 38.64; C, 28.25; H, 1.58; Cl, 13.89. The addition of 0.12 g. of KBr in 0.4 ml. of water to 0.15 g. of $[AuCl_2(phen)]Cl$ in 25 ml. of water gave 0.13 g. of a tan solid. *Anal.* Found: Au, 32.5. Calcd. for $AuBr_3C_{12}H_8N_2$: Au, 32.0.

$[AuCl_2(phen)][AuCl_4]$.—The addition of a solution of 0.42 g. of $HAuCl_4$ in 1 ml. of water to a solution of 0.4 g. of $[AuCl_2(phen)]Cl$ in 30 ml. of water gave 0.70 g. of a yellow precipitate. *Anal.* Found: Au, 50.3, 50.27; C, 18.57; H, 1.17; Cl, 27.17. Calcd. for $Au_2Cl_6C_{12}H_8N_2$: Au, 50.09; C, 18.31; H, 1.02; Cl, 27.01.

Acknowledgment.—We are indebted to Drs. H. A. Laitinen and C. E. Shoemaker for their generous assistance with the polarographic studies. The analyses were in large part made by the University of Illinois microanalysts and the Clark Microanalytical Laboratory.

CHICAGO, ILL. RECEIVED MARCH 15, 1951

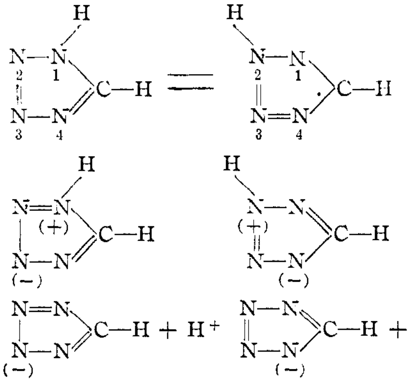
[CONTRIBUTION FROM THE RESEARCH LABORATORY OF THE U. S. NAVAL ORDNANCE TEST STATION]

The Heats of Combustion of Compounds Containing the Tetrazole Ring[1]

BY W. S. MCEWAN[1] AND M. W. RIGG[2]

The heats of combustion for some twenty-eight compounds related to tetrazole have been determined in order to provide fundamental knowledge of the average bond strength and resonance energy of this type of compound. By use of reported bond energies the resonance energy of the tetrazole ring is found to be between 55 and 70 kcal./ring depending upon substituent groups. Elimination of the tautomeric shift appears to increase rather than decrease the resonance energy of the tetrazole ring.

Tetrazole (CH_2N_4) is an interesting molecule since the combination of four atoms of nitrogen and one of carbon in a stable compound is seldom found. The stability of tetrazole is indicated by the relatively high melting point, 155°, without decomposition, and the relative stability of the compound in chemical reactions involving side groups, *i.e.*, the diazotization of 5-aminotetrazole and the oxidation of the phenyl group in phenyltetrazole. The apparent stability of the tetrazole ring indicates that a considerable resonance or stabilizing energy must be present in the system. This stability is undoubtedly due to the following factors: It is possible to have two tautomeric isomers, an ionized form (tetrazole is a weak acid, $K_a = 1.28 \times 10^{-5}$) which would have resonance stability, and the possibility of an electron shift within the molecule, with a resultant charge separation, which would also have resonance stability. The electron shift could be considered the first step in the ionization.



It should be pointed out, in this case, that substitution in the 1- or 2-position on the tetrazole ring removes the contribution of the tautomeric shift, and of the ionized form to the stabilization energy. Thus, the work presented here contains data on compounds from the following important groups: 5-substitutions, 1- or 2-substitutions, 1,5- and 2,5-disubstitutions. The 1-substituted compounds contain the conjugated system —N=N—N=C— whereas the 2-substituted compounds contain the conjugated system —N=N—C=N— and the two systems may not have identical stabilities.

A value of 30 kcal./mole for the resonance energy has been assumed in a number of calculations, although a recent reference (Elpern, THIS JOURNAL, **72**, 3379 (1950)) claims that tetrazole has little or no resonance energy. This statement is based upon the fact that tetrazole shows no absorption in the ultraviolet region. In order to obtain some additional information which might be used to estimate the resonance energy, the heats of combustion of tetrazole and a number of tetrazole derivatives were measured and the data combined with values for the heats of formation of water[3] and carbon dioxide[4] to obtain a value for the heat of formation of the various compounds. The calculations are based upon the formation of molecular nitrogen from the nitrogen in the sample.

Experimental

The calorimeter was similar to standard units which have been described by the Bureau of Standards. The unit was placed in a constant temperature water-bath, controlled to ±0.002°, as measured by a platinum resistance thermometer. The calorimeter was filled with the same quantity, ±0.1 g., of distilled water before each run. The cover to the calorimeter was designed in such a way that the thermostat stirrer forced a flow of water through the cover, thus completely enclosing the calorimeter in a constant temperature water jacket.

The standard Parr double valve bomb was used in all of these experiments. The samples, in the shape of a pellet (1.5 cm. dia., 0.5 cm. thick), and placed on a piece of fuse paper, were burnt in a small platinum crucible supported by one of the firing electrodes in an atmosphere of oxygen

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(1) Article not copyrighted.

(2) Temple University, Philadephia 22, Pennsylvania.

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TABLE I

Compound	Molecular formula	ΔH (Comb.) kcal./mole[b]	ΔH (Form.) kcal./mole at 25°
Tetrazole[8]	CH_2N_4	219.03 ± 0.21	56.66
1-Phenyltetrazole[9]	$C_7H_8N_4$	949.78 ± .36	86.47
5-Phenyltetrazole[10]	$C_7H_6N_4$	933.23 ± .33	69.91
1,5-Diphenyltetrazole[11]	$C_{13}H_{10}N_4$	1663.58 ± .52	99.32
2,5-Diphenyltetrazole[12]	$C_{13}H_{10}N_4$	1658.66 ± .51	94.40
1-Phenyl-5-methyltetrazole[11]	$C_8H_8N_4$	1096.26 ± .07	70.57
2-Phenyl-5-methyltetrazole[13]	$C_8H_8N_4$	1091.31 ± .14	65.62
1-Phenyl-5-hydroxytetrazole[14]	$C_7H_6N_4O$	890.02 ± .67	26.71
2-Phenyl-5-carboxytetrazole[15]	$C_8H_6O_2N_4$	947.46 ± .03	−9.91
1,5-Dimethyltetrazole[16]	$C_3H_6N_4$	532.19 ± .85	45.08
5-Aminotetrazole[8]	CH_3N_5	246.20 ± .56	49.67
5-Aminotetrazole nitrate[8]	$CH_4O_3N_6$	224.10 ± .45	−6.58
5-Nitroaminotetrazole[a]	$CH_2N_6O_2$	222.6 ±	60.3
Guanidine salt of 5-nitroaminotetrazole[17]	$C_2H_7O_2N_9$	453.80 ± 0.88	26.59
5-Guanylaminotetrazole[8]	$C_2H_5N_7$	399.46 ± .37	40.57
5-Acetamidotetrazole[8]	$C_3H_5N_5O$	451.74 ± .44	−1.81
5-Tetrazolylurethan[8]	$C_4H_7N_5O_2$	562.75 ± .65	−52.57
5,5′-Hydrazotetrazole[18]	$C_2H_4N_{10}$	459.87 ± 1.06	135.14
Benzalhydrazone of 5-hydrazinotetrazole[19]	$C_8H_8N_6$	1135.15 ± 0.22	109.46
Formazylbenzene[20]	$C_{19}H_{16}N_4$	2463.17 ± .25	129.54
Formazane[21]	$C_{13}H_{12}N_4$	1741.92 ± .25	109.34
1,3-Diphenyltetrazene[22]	$C_{12}H_{12}N_4$	1636.93 ± .39	98.41
2,2′-Hydrazo-bis-isobutyronitrile[23]	$C_8H_{14}N_4$	1259.16 ± 1.10	28.52
2,2′-Azo-bis-isobutyronitrile[24]	$C_8H_{12}N_4$	1216.95 ± 0.00	54.63
Di-aminoguanidine nitrate[25]	$C_1H_8N_6O_3$	329.76 ± .10	−37.56
Nitroaminoguanidine[26]	$CH_5N_5O_2$	270.14 ± .18	5.30
Nitroguanidine[27]	$CH_3O_3N_3$	208.6	
Guanylazide nitrate[28]	$CH_4N_6O_3$	234.48 ± .35	3.80
Nitroguanylazide[29]	$CH_2N_6O_2$	233.69 ± 1.02	71.32

[a] Calculated from guanidine salt. [b] ± values are mean deviations from the mean.

(40 atm.). The fuse paper was attached to a standard length of fuse wire, which was attached to the electrodes. The bomb was flushed three times with 30 atm. of oxygen and then filled to 30 atm. pressure for the calibrations with benzoic acid, and 40 atm. for the combustion of the samples. Corrections were made for the heat added to the bomb by the electrical current used to ignite the fuse wire, the burning of the fuse wire and fuse paper, carbon and nitric acid formation in the combustion, as well as the usual thermal leakage, stirring and pressure corrections.

Temperature measurements were made with a platinum resistance thermometer in conjunction with a Type G-2 Mueller resistance bridge and a sensitive galvanometer. The temperature rise in the calorimeter varied from about 1.000 to 3.000 ± 0.0003° depending upon the size, and heating value of the sample. Some of the materials studied could not be burnt in large samples, due to spattering and the formation of large amounts of carbon.

The energy equivalent of the calorimeter was determined by combustion of benzoic acid (National Bureau of Standards, Standard Sample 39f[5]).

Eight combustions of the standard benzoic acid (using approximately 1-g. samples) yielded a value of 2284.99 cal./deg. for the heat capacity of the calorimeter, with an average deviation of 0.025%. Corrections to standard condition were made by the method proposed by Washburn.[6]

Materials.—The following compounds were prepared by Dr. Ronald Henry[7]: tetrazole, 1-phenyltetrazole, 5-phenyltetrazole, 1,5-diphenyltetrazole, 2,5-diphenyltetrazole, 1-phenyl-5-methyltetrazole, 2-phenyl-5-methyltetrazole, 1-phenyl-5-hydroxytetrazole, 2-phenyl-5-carboxytetrazole, 1,5-dimethyltetrazole, 5-aminotetrazole, 5-aminotetrazole nitrate, guanidine salt of 5-nitroaminotetrazole, 5-guanylaminotetrazole, 5-acetamidotetrazole, 5-tetrazolylurethan, 5,5′-hydrazotetrazole, benzalhydrazone of 5-hydrazinotetrazole, formazylbenzene, formazane, 1,3-diphenyltetrazene, 2,2′-azobisisobutyronitrile, 2,2′-hydrazobisisobutyronitrile, diaminoguanidine nitrate, nitroaminoguanidine, nitroguanidine, guanylazide nitrate, nitroguanylazide. The compounds were purified by recrystallization, and purity checked by the constancy of melting points upon successive recrystallizations. The densities of the materials were estimated from the dimensions and weight of the pellets. Three to five combustions were made with each compound studied.

The values for the heats of combustion and formation are listed in Table I.

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Discussion

The resonance energy for the tetrazole ring was calculated by combining our experimentally determined heats of combustion and heats of sublimation[30] with reported bond energy values[31] for four cases: tetrazole, 1,5-dimethyltetrazole, 1,5-diphenyltetrazole, 2,5-diphenyltetrazole. In these calculations, the C–N bond was assumed to be the standard type bond. Accurate information concerning bond energies in a molecule such as tetrazole is not available at this time. In considering the diphenyltetrazoles, the resonance energy of the phenyl groups was assumed to be additive and to have a value of 41 kcal. per phenyl ring. The resonance energies calculated for the four compounds were 55.6, 61.3, 65 and 70.3 kcal. per tetrazole ring, respectively. These values indicate that the resonance energy of the tetrazole ring is increased by the elimination of the tautomeric shift. This is an interesting point and should be investigated further. It will also be noted that the 2,5-disubstituted tetrazoles are more stable, 5 kcal. per mole, than the corresponding 1,5-disubstituted isomers (2 cases).

It would be of interest to have a larger number of 1,5- and 2,5-isomers to compare, and also to obtain additional sublimation data for the calculation of resonance energies. The comparison of the data in Table II again indicates the relative stability of compounds containing four nitrogen atoms in a ring compared to the isomeric non-cyclic structure.

TABLE II

	ΔH_c	ΔH_f
Nitroguanylazide	233.69	71.3
5-Nitroaminotetrazole	222.1 calcd.	59.7
Calcd. from guanidine salt	222.6	
Guanylazide nitrate	234.5	3.8
5-Aminotetrazole nitrate	224.1	−6.6
1,5-Diphenyltetrazole	1663.6	99.3
2,5-Diphenyltetrazole	1658.7	94.4
Formazane	1741.9	109.3

CHINA LAKE, CALIF.

RECEIVED MARCH 30, 1951

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(30) Dr. F. M. Ernsberger and Mr. John Wiley of this Laboratory very kindly measured the vapor pressures of tetrazole, 1,5-diphenyltetrazole and 2,5-diphenyltetrazole for us by means of the Knudsen effusion technique. They found the following expressions to hold over the temperature range indicated:

for tetrazole

$$\log_{10}P = \frac{-5090}{T} + 15.79 \qquad (60\text{–}90°)$$

for 1,5-diphenyltetrazole

$$\log_{10}P = \frac{-6360}{T} + 17.20 \qquad (75-90°)$$

for 2,5-diphenyltetrazole

$$\log_{10}P = \frac{-6250}{T} + 18.32 \qquad (60\text{–}80°)$$

From these expressions ΔH's for sublimation were calculated to be:

tetrazole ΔH_S = 23.26 kcal./mole
1,5-diphenyltetrazole ΔH_S = 29.05 kcal./mole
2,5-diphenyltetrazole ΔH_S = 28.60 kcal./mole

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[CONTRIBUTION FROM THE CRYOGENIC LABORATORY AND THE DEPARTMENT OF CHEMISTRY, THE OHIO STATE UNIVERSITY]

The Vapor Pressures of Inorganic Substances. VI. Vanadium Between 1666°K. and 1882°K.[1]

BY JAMES W. EDWARDS, HERRICK L. JOHNSTON AND PAUL E. BLACKBURN

The vapor pressure of vanadium was determined over the temperature range 1666° to 1882°K. by measuring the rate at which a metal surface evaporates into a vacuum. Values of ΔH_0° were calculated from individual vapor pressures and showed no appreciable trend, the average value being 121.95 ± 0.14 kcal. By combining this value with a linear expression in T for the difference in free energy functions between solid and gaseous vanadium, the following vapor pressure equation was obtained: $R \ln p = \frac{-121.95 \times 10^3}{T} - 5.123 \times 10^{-4}\, T + 36.29$.

Introduction

The vapor pressure of vanadium has been determined in this Laboratory by the method first introduced by Langmuir[2] and later modified by Marshall, Dornte and Norton.[3] This method consists of measuring the rate at which a metal evaporates in a vacuum from a ring or cylinder heated to a constant temperature by radiofrequency induction.

Experimental Method

Apparatus and Procedure.—The techniques and apparatus we used are essentially similar to those described in earlier papers from this Laboratory.[4]

In the present investigation the Pyrex apparatus used was the same as that described in reference.[4e] The procedure was modified in two ways: (1) The apparatus was not sealed off from the diffusion and fore-pumps. (2) The optical pyrometer was calibrated after each run with the optical window in the line of sight, so as to determine the small temperature error introduced by condensation of metal on the window. This correction was negligible for the low temperature runs and reached a maximum value of 14° for the highest temperature runs. For a given run, the correction was assumed to be proportional to the time-at-high-temperature of the sample, since the shutter was opened for temperature readings at uniform time intervals.

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(1) This work was supported in part by The Office of Naval Research under contract with The Ohio State University Research Foundation.

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