[CONTRIBUTION FROM THE RICHARDSON CHEMICAL LABORATORY, TULANE UNIVERSITY]

The Heats of Combustion of Diazoaminobenzene, Benzotriazole and 2-Triazoethanol

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RECEIVED FEBRUARY 17, 1953

The ΔE's of combustion at 298.1°K. of diazoaminobenzene, benzotriazole and 2-triazoethanol were found to be $1582.7_8 \pm 0.31$, $794.9_7 \pm 0.21$, and $381.9_2 \pm 0.38$ kcal. per mole, respectively. From these the enthalpies of formation from the elements and from the gaseous atoms have been calculated. The resonance energies of diazoaminobenzene and benzotriazole have been estimated.

In connection with a study of the physical properties of some triazo compounds[1] in this Laboratory, it seemed of interest to determine the heats of combustion of some of these compounds and of similar compounds containing three adjacent nitrogen atoms. Since the structural properties of the N_3 group in each of the three compounds selected are known to be different, the energy relationships should be different also.

Experimental

Preparation and Purification of Materials.—The diazoaminobenzene, an Eastman Chemical Company "White Label" product, was recrystallized fractionally several times from a 60% methanol–water solution and stored under reduced pressure in complete darkness. To prevent contamination of the sample by decomposition products, all calorimetric measurements were made within three days after purification of the compound. Of the six determinations reported, two were made on each of three separately recrystallized fractions. Agreement among the measurements on the three separate fractions was taken as satisfactory proof that the compound was pure. In fact, the heat of combustion was a more sensitive test of purity than the melting point.

The benzotriazole, an Eastman Chemical Company "White Label" product, was fractionally crystallized from C.P. grade benzene several times and dried in a vacuum oven at 65°. Two samples each from three separately recrystallized batches were used in the measurements.

The 2-triazoethanol was prepared, with modifications, according to the method described by Forster and Fierz.[2] Fifty grams of sodium azide, mixed with an equal weight of ethylene chlorohydrin, was heated on a steam-bath for 48 hours. The contents were filtered and washed with ether. The ether was removed from the product by heating at a temperature of 100° under 70 mm. pressure for 30 minutes. The temperature of the bath was then lowered to about 60° and the pressure reduced to 1–2 mm. At this pressure the compound distilled at 31°. An ebulliator was used to prevent bumping. The triazoethanol was freshly distilled before each determination. A nearly constant refractive index (±0.0001) for successive constant boiling fractions was considered evidence for the purity of the compound.

Apparatus and Procedure.—The Parr Adiabatic Oxygen Bomb Calorimeter was used in this investigation. The bomb, made of a special nickel chromium steel alloy, had a self-sealing head. The volume of the bomb was 0.360 liter.

A nickel–chromium alloy wire of known calorific value was used to ignite the samples. The temperature rise in the bucket was measured with a Beckmann thermometer, calibrated against a Parr thermometer which was used to measure the temperature of the jacket. The latter thermometer was calibrated by the National Bureau of Standards. The weight of the water (2000 g.) added to the bucket containing the bomb was corrected to "*in vacuo*."

On the completion of a combustion the bomb was removed and the gaseous products bubbled through a dilute solution of sodium carbonate containing modified methyl orange as indicator. When the pressure of the bomb reached atmospheric pressure the bomb was disassembled and the contents and all inside surfaces washed with distilled water containing the indicator. The collected wash waters were added to the solution and the amount of nitric acid formed from the combustion determined by titrating with a standard solution of sodium carbonate. This solution was so prepared that one milliliter corresponded to one calorie of heat released in the formation of aqueous nitric acid. This was calculated from the value for the heat of formation of nitric acid (aqueous) as reported by Jessup,[3] namely, 14.345 kcal. per mole.

The calorimeter was standardized by burning a standard sample of benzoic acid, using the latest value for the heat of combustion of benzoic acid as reported by Parks[4] and correcting to the conditions of the bomb according to the corrections listed by Jessup.[3] This value, 26,429.4 joules per gram, corrected to the conditions of the bomb, becomes 26,449.4 joules per gram or 6322.5 cal. per gram (using the conversion factor of 4.1833 cal. per joule). The values for the energy equivalent of the calorimetric system at 25° in five determinations were 2501.31, 2502.07, 2502.10,[5] 2501.88 and 2500.95. The average value, 2501.7 ± 0.42, was used in the calculations of this investigation.

Considerable difficulty was experienced in the early attempts to ignite diazoaminobenzene. The use of a stainless steel cup to hold the sample pellets, under an initial oxygen pressure of 30 atmospheres, resulted in incomplete combustion in all trials. The substitution of a platinum crucible, insulated thermally from its support by a thin wrapping of tightly twisted glass wool (Pyrex), effected rapid and complete combustion under the proper oxygen pressure. Initial oxygen pressures above 28 atmospheres gave erratic results due to incomplete combustion. In experiments carried out at an initial pressure of 25 atmospheres complete combustion was obtained in all trials. After the bomb, with sample, was introduced into the bucket, the temperature of the jacket was adjusted to that of the bucket water and the entire system allowed to come to thermal equilibrium. Usually an equilibration period of at least one-half hour was sufficient. It was found that if the equilibration period extended over a period of 1.5 hours or more, the heat of combustion of the diazoaminobenzene was appreciably higher than usual, and the increase in the number of calories released by the combustion was a function of the time that the sample was under the influence of the water vapor (from the water added to the bomb to absorb HNO_3) and the high-pressure oxygen. Inspection of the unignited sample, after a period of 2.5 hours under high pressure showed only slight, but perceptible, discoloration.

The 2-triazoethanol was placed in spherical glass bulbs, which in turn were supported by the stainless steel crucible. Richards and Barry[7] reported that for liquid samples the bulbs should have thin walls, partially collapsed, and be filled completely. In this manner the liquid supports the pressure of the oxygen introduced in the bomb. Because of the low coefficient of expansion and low vapor pressure of the compound, bulbs were filled with difficulty by this technique and invariably broke under pressures of from 5 to 7 atmospheres. Spherical bulbs weighing about 0.30 g. with fairly thick walls proved most satisfactory. With such bulbs, when combustion was complete, the glass was shattered to a completely pulverized state. If the bulb was too

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(1) H. O. Spauschus and J. M. Scott, THIS JOURNAL, **73**, 208, 210 (1951).

(2) M. O. Forster and H. E. Fierz, *J. Chem. Soc.*, **93**, 1865 (1908).

(3) R. S. Jessup, *J. Research Natl. Bur. Standards*, **29**, 247 (1942).

(4) G. S. Parks, *J. Chem. Phys.*, **18**, 152 (1950).

(5) This trial was made using a constant temperature bath instead of the adiabatic jacket, the true temperature rise being determined by the standard rating period method described by White.[6]

(6) W. P. White, "The Modern Calorimeter," The Chemical Catalog Co., Inc., Reinhold Publ. Corp., New York, N. Y., 1928.

(7) T. W. Richards and F. Barry, THIS JOURNAL, **37**, 993 (1915).

TABLE I

Trial	Wt. sample, g.	Δp, atm.	Δt, °C.	M_{HNO_3}	$-\Delta U_B$ (298°K.), kcal./mole	Cor., %	$-\Delta U_R$ (298°K.) kcal./mole
				Diazoaminobenzene			
1	0.4327	−0.564	1.404	0.000752	1583.99	−0.1154	1582.16
2	.5132	− .667	1.662	.000909	1584.71	− .1190	1582.87
3	.4131	− .671	1.340	.000763	1584.99	− .1185	1583.16
4	.3690	− .483	1.198	.000711	1584.32	− .1169	1582.50
5	.3171	− .415	1.031	.000587	1584.84	− .1159	1583.03
6	.4610	− .610	1.495	.000987	1584.82	− .1177	1583.00
						Av.	1582.78 ± 0.31
				Benzotriazole			
1	0.4695	−0.517	1.265	0.000866	795.79	−0.1104	794.91
2	.6183	− .677	1.665	.001114	796.10	− .1116	795.21
3	.6995	− .770	1.884	.001304	795.94	− .1120	795.05
4	.5789	− .655	1.560	.001240	796.04	− .1104	795.16
5	.4735	− .519	1.276	.000950	795.27	− .1107	794.39
6	.4936	− .546	1.331	.000987	795.99	− .1104	795.11
						Av.	794.97 ± 0.21
				2-Triazoethanol			
1	0.9838	+0.4660	1.718	0.003196	382.21	−0.1037	381.81
2	.6143	.2915	1.075	.001988	383.13	− .1061	382.72
3	.6078	.2885	1.058	.001774	381.94	− .1041	381.54
4	.6340	.3005	1.105	.001850	382.49	− .1042	382.09
5	.6298	.2995	1.099	.001940	381.95	− .1027	381.46
						Av.	381.92 ± 0.38

thin, it cracked before ignition; if too thick, combustion was incomplete and the fragments of glass relatively large. Attempts to use benzoic acid pellets with the sample to start ignition were unsuccessful.

The precision of the measurements of the heat of combustion of the triazoethanol was lower than that of the other two reported here because of the violence of the explosive combustion. A sample weighing about 0.6 g. produced a temperature rise of a little over one degree; yet this sample burned with sufficient explosiveness to force the stainless steel cup through its ring support, invert it, and throw it to the bottom of the bomb with sufficient force to leave a permanent circular imprint there. The bottom of the cup was itself bent inward approximately one millimeter; the entire calorimeter was shaken visibly (and audibly) on the ignition of the sample.

Results and Calculations.—The decrease in intrinsic energy for each of the combustion reactions was calculated with the aid of the equation of Washburn[8] and modified to apply to these nitrogen-containing compounds. In the calculations of the effective heat capacity of the initial and final systems the nitrogen was treated as oxygen, according to the suggestion of Washburn. Atomic weights used were those reported by Wichers.[9] The symbols are those of Washburn. Data and derived results are listed in Table I. The fifth column of Table I lists M_{HNO_3}, the number of gram-formula-weights of HNO_3 formed from the nitrogen. This quantity varied with the compound and the weight of each sample and accordingly had to be measured with each combustion.

The average value of $-\Delta U_R$ is the thermodynamic quantity ΔE. The formula $\Delta H = \Delta E + \Delta nRT$ was used to change from internal energy to enthalpy. The values of Δn, the difference between the number of moles of gaseous products and the number of moles of gaseous reactants, per mole of compound consumed in the combustion, are 1/4, −5/4 and 3/4 for benzotriazole, diazoaminobenzene and triazoethanol, respectively. The correction of ΔH to zero pressure was made with the use of the values 2.0 cal. per mole and 10.3 cal. per mole, for $O_2(g)$ and $CO_2(g)$, respectively, as reported by Rossini.[10] The values for ΔH of combustion calculated for benzotriazole, diazoaminobenzene and 2-triazoethanol are −794.76, −1583.39 and −381.36 kcal., respectively. The mean deviations are ±0.21 kcal. for benzotriazole, ±0.306 kcal. for diazoaminobenzene, and ±0.38 kcal. for 2-triazoethanol. The average deviation from the mean, defined by $[\Sigma d^2/n(n-1)]^{1/2}$ where d is the deviation of an individual measurement from the mean and n is the number of measurements, was found to be 0.156 kcal. for diazoaminobenzene, 0.124 kcal. for benzotriazole and 0.225 kcal. for 2-triazoethanol.

Discussion

The enthalpies of formation, at 298°K., of the compounds from their elements were calculated with the use of the data from Rossini[11]

$$3/2\ N_2(g) + 11/2\ H_2(g) + 6C(gr) = C_{12}H_{11}N_3(s) \qquad \Delta H^0_{f298} = +79.03 \text{ kcal.} \quad (1)$$

$$3/2\ N_2(g) + 5/2\ H_2(g) + 6C(gr) = C_6H_5N_3(s) \qquad \Delta H^0_{f298} = +59.66 \text{ kcal.} \quad (2)$$

$$3/2\ N_2(g) + 1/2\ O_2(g) + 2C(g) = C_2H_5ON_3(l) \qquad \Delta H^0_{f298} = +22.47 \text{ kcal.} \quad (3)$$

The enthalpies of formation of diazoaminobenzene and benzotriazole from the gaseous elements in the atomic state were found to be

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(8) E. W. Washburn, *J. Research Natl. Bur. Standards*, **10**, 525 (1933).

(9) E. Wichers, THIS JOURNAL, **74**, 2447 (1952

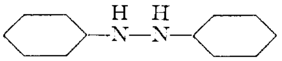
(10) F. D. Rossini, *J. Research Natl. Bur. Standards*, **22**, 407 (1939).

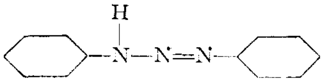
(11) F. D. Rossini, "Selected Values of Chemical Thermodynamic Properties," National Bureau of Standard, Circular 500, Washington, D. C., 1950.

$$12C(g) + 11H(g) + 3N(g) = C_{12}H_{11}N_3(s) \qquad \Delta H_{298} = -2812.1 \text{ kcal.} \quad (4)$$

$$6C(g) + 5H(g) + 3N(g) = C_6H_5N_3(s) \qquad \Delta H_{298} = 1488.7 \text{ kcal.} \quad (5)$$

The determination of the stabilization energy of the three nitrogen groups in each of these compounds can be made only after a careful estimation of the contributions of the bond energy terms for the N-H, N-N and N=N bonds. To do this, the method of Gilbert and Anderson[12] was applied to the compounds


(6)


(7)

It is obvious that the energy of formation of hydrazobenzene (6) differs from that of diazoaminobenzene (7) chiefly by the energy of one N-H bond, the energy of one -N-N- bond, the energy of =N-N- bond and the energy of one -N=N- bond. The heat of formation of hydrazobenzene from the gaseous atoms is given by

$$12C(g) + 12H(g) + 2N(g) = C_{12}H_{12}N_2(s) \qquad \Delta H_{298} = -2804.4 \text{ kcal.} \quad (8)$$

The values of the bond energy terms taken from the work of Cole and Gilbert,[13] are listed below with the parent compounds from which they were determined.

Bond	Bond energy term, kcal.	Parent compound
D(N—H)	88.0	Hydrazine
D(—N—N—)	33.7	Hydrazobenzene
F(—N=N—)	−82.7	*p*-Aminoazobenzene
F(=N—N—)	−45.1	Phenylhydrazine

D( ) refers to the dissociation of the bond and F( ) to the formation of the bond. With the use of these values and equation (5) the heat of formation of diazoaminobenzene is calculated to be

$$12C(g) + 11H(g) + 3N(g) = C_{12}H_{11}N_3(s) \qquad \Delta H_{298} = -2810.5 \text{ kcal.} \quad (9)$$

The value of 2810.5 kcal. per mole obtained from these calculations compares favorably with the value computed from the observed heat of combustion and justifies the use of Cole and Gilbert's bond energy terms in conjunction with the bond energy terms of Wheland[14] in the calculation of the stabilization energy of diazoaminobenzene. However, the values of Wheland, based in part on the calculation of Pauling,[15] were derived by use of a value of 124.3 kcal. per gram atom for the heat of sublimation of graphite rather than the value 171.7 kcal. per gram atom used in the above calculations. Recalculation on the basis of Wheland's values gives for equation (9)

$$12C(g) + 11H(g) + 3N(g) = C_{12}H_{11}N_3(s) \qquad \Delta H_{298} = -2239.0 \text{ kcal.} \quad (10)$$

Using a heat of sublimation for diazoaminobenzene, estimated to be the same as that for hydrazobenzene, of 20.0 kcal. per mole one obtains

$$12C(g) + 11H(g) + 3N(g) = C_{12}H_{11}N_3(g) \qquad \Delta H_{298} = -2219.0 \text{ kcal.} \quad (11)$$

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(12) G. M. Anderson and J. B. Gilbert, THIS JOURNAL, **64**, 281 (1942).

(13) L. C. Cole and E. C. Gilbert, *ibid.*, **73**, 5423 (1951).

(14) G. W. Wheland, "The Theory of Resonance," Chap. 3, J. Wiley and Sons, Inc., New York, N. Y., 1944.

(15) L. Pauling, "The Nature of the Chemical Bond," 2nd Ed., Cornell University Press, Ithaca, N. Y., 1940.

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, UNIVERSITY OF MARYLAND]

Carbonyl Reactions. I. The Kinetics of Cyanohydrin Formation in Aqueous Solution[1]

BY W. J. SVIRBELY AND JAMES F. ROTH[2]

RECEIVED NOVEMBER 26, 1952

The kinetics of the formations of the cyanohydrins of acetaldehyde, propionaldehyde and acetone have been studied in dilute aqueous solution at 25°. Measurements were conducted in acetate buffers under various conditions to ascertain the influence of ionic strength, *p*H and buffer composition on the rate constants. The following results were obtained: (1) the reactions of these carbonyl compounds with HCN follow a second-order equation; (2) the kinetic salt effect is quite small; (3) acetaldehyde and propionaldehyde react quantitatively with HCN whereas acetone does not; (4) general catalysis was not detected for either acetone or acetaldehyde cyanohydrin formation; (5) in the propionaldehyde reaction a small general catalytic effect is indicated. It is shown that in the absence of general catalysis there are a number of different mechanisms which are equally consistent with the experimental rate equation. On the basis of the kinetics alone, with or without general catalysis, there is no justification for preferring the Lapworth mechanism. A consistent mechanism for carbonyl addition reactions is proposed.

Introduction

The generally accepted mechanism for cyanohydrin formation is based on the qualitative studies of Lapworth.[3] The mechanism is

$$AO + CN^- \xrightarrow{\text{slow}} A(CN)O^-$$
$$A(CN)O^- + H^+ \xrightarrow{\text{fast}} A(OH)(CN) \quad (1a)$$

The above mechanism does not involve catalysis in the sense that there is either a protolytic reaction between a catalyst and the carbonyl molecule or formation of an intermediate complex between these two entities. This feature of the mechanism is surprising when one considers that other carbonyl

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(1) (a) Abstracted from a thesis submitted by James F. Roth to the Graduate School of the University of Maryland in partial fulfillment of the requirements for the degree of Doctor of Philosophy; (b) presented in part at the New York City Meeting of the International Congress of Chemistry, September, 1951.

(2) National Institutes of Health Research Fellow, 1950-1951.

(3) A. Lapworth, *J. Chem. Soc.*, **83**, 995 (1903); **85**, 1206 (1904).