The Heats of Combustion and Formation of the Three Diazines and their Resonance Energies

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Heat of combustion values have been determined for pyridazine, pyrimidine and pyrazine and found to be, $\Delta Hc°(25°C)$ in kcal.mole^{-1}, -566.59 ± 0.22, -547.88 ± 0.20 and -546.25 ± 0.28, respectively, and heat of formation data are derived. From these values the resonance energies of the diazines have been calculated and the implication on certain thermochemical bond energy terms is discussed.

It is generally accepted that a high degree of stabilization of a simple aromatic system is mainly due to the fact that at least two of the possible valence-bond structures are indistinguishable, as are the Kekulé-structures of benzene. Amongst the six-membered, aromatic heterocyclic ring systems with one or several nitrogen atoms in the ring, pyridine has identical Kekulé-structures. Of the three isomeric diazines, the 1,4- and 1,3-isomers, pyrazine and pyrimidine, respectively, are analogous with pyridine, whereas the 1,2-isomer, pyridazine, has energetically quite different structures (Fig. 1).

It was therefore expected that a determination of the heats of combustion of the three isomers should reveal a considerable difference in the derived resonance stabilization energies — the 1,3- and 1,4-diazines being more stable than the 1,2-isomer.

MATERIALS

Pyridazine. A 40 g sample was kindly provided by Dr. Clauson-Kaas [1], Copenhagen. GLC-analysis (Pye Argon Chromatograph, column: 20 % LAC 3R-728 on C22, $t = 150°$) showed only one minor impurity. Two successive fractional distillations at 94.0° and 16 mm and at 84.0° and 10 mm, gave a product that was free from impurities as judged from the GLC-analysis ($d_4^{25} = 1.1030$).

Pyrimidine. 2-Amino-pyrimidine (Light) was chlorinated to 2-chloropyrimidine as described by Overberger and Kogon [2]. The product was hydrogenated using Pd on $BaSO_4$ as catalyst following the method of Lythgoe and Rayner [3]. The product obtained contain-
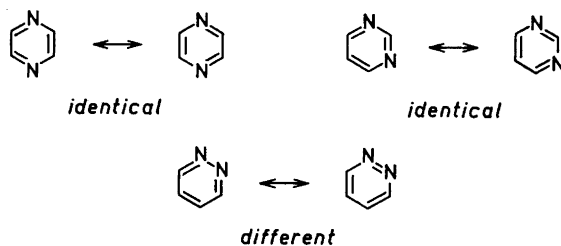

Fig. 1.

ed much water. Separation could be achieved by distillation neither at 760, nor at 100 mm Hg due to formation of azeotropic mixtures (ca. 2 % H_2O). After successive treatments with KOH and P_2O_5, as described by Whittaker[4], the substance was distilled twice (60°/89 mm and 122.8°/746 mm). A product was obtained which contained less than 0.01 % H_2O as judged from the GLC-analysis (column as above, $t = 100°$). $d_4^{25} = 1.0792$.

Pyrazine. Wyandotte Chem. Corp., Wyandotte, USA, kindly provided a 120 g sample of pyrazine of very high quality. Two distillations over $CaSO_4$ followed by a vacuum sublimation gave a product that was free from impurities to within one part in 10^4 as judged from GLC (column as above, $t = 114°$, the sample was dissolved in neohexane). M.p. 54.0°, b.p. 116.0° at 760 mm.

COMBUSTION CALORIMETRY

The calorimetric results are expressed in terms of the defined calorie which is equal to 4.1840 abs.joules. All weighings have been reduced to mass. The molecular weights are based upon the 1957 International Atomic Weights. The symbols introduced by Hubbard, Scott and Waddington[5] (and their method of performing the Washburn reduction) have been used.

Apparatus and method. The same combustion calorimeter[6] was used as in previous investigations. Due to a minor change in the head of the bomb two different values of the heat equivalent of the system were used. The calibration experiments reported in this work refer to the combustion of pyrimidine and pyrazine. The heat equivalent value used for the combustions of pyridazine was the same as has been reported elsewhere[6].

Pyridazine and pyrimidine, being liquids, were burnt in soft glass ampoules with paraffin oil as combustion aid. For the solid pyrazine soft glass ampoules were used, each of which had a 3 mm hole in its bottom face through which the molten substance could be introduced. After solidification of the substance, the ampoule was placed in a specially designed platinum crucible, with a depression in the bottom, fitting the base of the ampoule. Experiments showed that no measurable loss of weight occurred during weighing and assembling operations. Enough paraffin oil was added to prevent a direct contact between the oxygen atmosphere and the substance. Therefore, the amount of paraffin oil had to be rather high, accounting for ca. 60 % of the heat evolved in the combustion. The analysis for HNO_3 were performed in the usual manner[7].

Table 1. Calibration, Benzoic acid NBS 39h. $\Delta E_c/M$(Benzoic acid) $= -6317.88 \pm 0.72$ cal.g^{-1}. m(Pt) $= 23.847$ g, ε^i(cont) $= 3.95$ cal.deg^{-1} (Expts. Nos. 1—5), ε^i(cont) $= 3.94$ cal.deg^{-1} (Expts. Nos. 6—9).

m' g	m'' g	m^i(cont) g	Δt deg	ΔE(HNO$_3$) cal	ε°(calor) cal.deg^{-1}
0.825757	0.005474	36.65	0.88851	2.52	5931.63
0.827198	0.005288	36.65	0.88999	1.69	5930.29
0.827939	0.005227	36.66	0.89091	2.37	5929.94
0.826054	0.005159	36.65	0.88889	2.49	5929.78
0.825815	0.005214	36.65	0.88856	2.02	5929.98
0.826013	0.005102	36.42	0.88836	1.96	5931.93
0.827279	0.005474	36.42	0.89027	2.07	5930.04
0.826546	0.005369	36.42	0.88931	1.92	5930.56
0.825211	0.005362	36.42	0.88783	2.21	5931.18
			Mean		5930.59
			Stand. dev. of mean		0.27

ε°(calor) $= 5930.59 \pm 0.27$ cal.deg^{-1}

Table 2. Pyridazine
Series 1: ε°(calor) $= 5927.63 \pm 0.24$ cal.deg^{-1},
  m(Pt) $= 28.047$ g, ε^i(cont) $= 4.01$ cal.deg^{-1}, $\Delta E\Sigma = 2.50$ cal.
Series 2: ε°(calor) $= 5925.67 \pm 0.24$ cal.deg^{-1},
  m(Pt) $= 23.689$ g, ε^i(cont) $= 3.88$ cal.deg^{-1}, $\Delta E\Sigma = 2.50$ cal.

m' g	m'' g	m''' g	m^i(cont) g	Δt deg	ΔE(HNO$_3$) cal	$-\Delta E_c^\circ/M$ cal.g
Series 1:						
0.446570	0.182024	0.005480	40.52	0.88219	12.10	7078.24
0.464177	0.175235	0.005587	40.53	0.89079	13.03	7076.65
0.495686	0.150052	0.005398	40.52	0.88122	12.99	7072.86
0.494709	0.150669	0.005311	40.52	0.88165	15.86	7073.15
0.475463	0.166085	0.005853	40.53	0.88747	12.52	7077.84
Series 2:						
0.554773	0.111482	0.005762	36.24	0.88058	15.52	7072.84
0.565616	0.108593	0.004938	36.21	0.88741	14.84	7071.62
0.528986	0.135143	0.005489	36.20	0.89290	13.04	7070.34
				Mean		7074.19
				Stand. dev. of mean		1.02

$\Delta E_c^\circ/M = -7074.2$ cal.g^{-1}

The combustions are reported in Tables 1—4. All combustion series had in common the following data: $t_h = 25.0°C$, $t_i = 24.1°C$, P^i(Gas) $= 30.0$ atm, V(Bomb) $= 0.2751$ l, V^i(Water) $= 0.820$ ml, $\Delta E_c^\circ/M$(Oil) $= -10\,986.6 \pm 0.6$ cal.g^{-1} and $\Delta E_c^\circ/M$(Fuse) $= -3\,971 \pm 4$ cal.g^{-1}.

Results. The values of $\Delta E_c^\circ/M$ obtained were recalculated to ΔH_c° values. The heats of formation for the compounds were calculated using the standard values for the heats of formation of gaseous CO$_2$[8] and liquid H$_2$O[8], -94.05

Table 3. Pyrimidine
$\varepsilon°(\text{calor}) = 5930.59 \pm 0.27 \text{ cal.deg}^{-1}$, $m(\text{Pt}) = 23.841$ g,
$\varepsilon^i(\text{cont}) = 3.88 \text{ cal.deg}^{-1}$, $\Delta E\Sigma = 2.45$ cal.

m' g	m'' g	m''' g	$m^i(\text{cont})$ g	Δt deg	$\Delta E(\text{HNO}_3)$ cal	$-\Delta E_c^°/M$ cal.-g^{-1}
0.454531	0.196203	0.005298	36.35	0.89895	12.87	6842.64
0.475318	0.180673	0.005320	36.35	0.89426	13.38	6842.89
0.432193	0.208901	0.005281	36.33	0.89629	12.05	6839.31
0.444418	0.203413	0.005604	36.33	0.90063	13.41	6838.49
0.447074	0.197778	0.004737	36.34	0.89249	11.89	6840.03
				Mean		6840.67
				Stand. dev. of mean		0.89

$\Delta E_c^°/M = -6840.7 \text{ cal.g}^{-1}$

Table 4. Pyrazine
$\varepsilon°(\text{calor}) = 5930.59 \pm 0.27 \text{ cal.deg}^{-1}$, $m(\text{Pt}) = 14.048$ g,
$\varepsilon^i(\text{cont}) = 3.53 \text{ cal.deg}^{-1}$, $\Delta E\Sigma = 2.50$ cal

m' g	m'' g	m''' g	$m^i(\text{cont}$ g	Δt deg	$\Delta E(\text{HNO}_3)$ cal	$-\Delta E_c^°/M$ cal.g^{-1}
0.298442	0.309073	0.003997	26.46	0.92455	13.88	6815.53
0.349285	0.284236	0.004562	26.46	0.93772	15.01	6817.76
0.339109	0.255077	0.004585	26.46	0.87171	13.81	6820.34
0.329619	0.258763	0.004095	26.46	0.86745	14.12	6822.48
0.293195	0.291620	0.004329	26.46	0.88664	13.25	6825.29
0.293809	0.309140	0.004337	26.46	0.91968	13.12	6820.55
				Mean		6820.32
				Stand. dev. of mean		1.40

$\Delta E_c^°/M = -6820.3 \text{ cal.g}^{-1}$

Table 5. Thermochemical data at 25°C, in kcal.mole^{-1}. The given uncertainties are twice the final overall standard deviations [10].

Compound	$\Delta H_c^°$	$\Delta H_f^°$	$\Delta H_c(\text{gas})$	$\Delta H_f(\text{gas})$
Pyridazine	-566.59 ± 0.22	53.75 ± 0.22	-579.37 ± 0.30	66.53 ± 0.30
Pyrimidine	-547.88 ± 0.20	35.04 ± 0.20	-559.83 ± 0.24	46.99 ± 0.24
Pyrazine	-546.25 ± 0.28	33.41 ± 0.28	-559.70 ± 0.36	46.86 ± 0.36

kcal.mole^{-1} and -68.32 kcal.mole^{-1}, respectively. Final overall standard devia-
tions were calculated by the method of Bjellerup [9] based upon the principles
of Rossini and Deming [10]. The heat of sublimation of pyrazine and the heat
of vaporization of pyrimidine were measured and found to be $13.4_5 \pm 0.11$
and $11.9_5 \pm 0.06$ kcal.mole^{-1}, respectively, using the apparatus and technique
described by Wadsö [11]. For pyridazine this method could not be used and

Table 6. Atomic heats of formation and resonance energies in kcal.mole⁻¹.

Compound	$-\Delta H_a$ calculated	$-\Delta H_a$ found	$\Delta H_{Res.}$
Benzene	1277.4	1318.2	40.8
Pyridine	1170.1	1194.3	24.2
Pyridazine *	1038.8 *	1051.1	12.3
Pyrimidine	1062.8	1070.8	8.0
Pyrazine	1062.8	1070.9	8.1

* The valence bond structure with a $N-N$ single bond.

therefore a preliminary value for the heat of vaporization, 12.78 ± 0.10 kcal.mole⁻¹, was obtained using a different and more sensitive method *. The results are summarized in Table 5.

RESONANCE ENERGIES

According to standard procedure, the thermochemical resonance energy for a conjugated system equals the difference between the calculated heat of combustion (or formation) value for the most stable valence-bond structure of the molecule and the experimentally determined value. The calculation rests upon the assumption that thermochemical bond energy terms are additive, which is only approximately true. However, by introducing structural refinements the agreement between calculation and experiment for molecules with localized bond orbitals can be as close as a few tenths of a kcal per mole. Table 6 gives the calculated and the experimentally determined atomic heats of formation for benzene [12], pyridine [13] and the three diazines using bond energy terms and heat of atomization values from Cottrell [14]. For pyridazine, the calculated values become 1 038.8 and 1 014.6 kcal.mole⁻¹ for the valence bond structures with $N-N$ and $N=N$ bonds, respectively, and the most stable one should be chosen for the comparison.

DISCUSSION

From Table 6 two rather surprising facts emerge. Firstly, that upon substituting a $-N=$ for a $-CH=$ group the resonance energy decreases by as much as 16 kcal per mole, and secondly, that the resonance energy of pyridazine — contrary to all expectations — is higher than those of the 1,4- and 1,3-isomers.

The regular decrease in resonance energy is very questionable and is certainly not supported by chemical evidence. One might even expect *sym*-triazine to show up in the calculation with a negative stabilization energy, which does not make sense at all. Pauling [15] states that the resonance energy

in pyridine, pyrazine and related six-membered heterocyclic molecules stabilizes them by about 40 kcal.mole^{-1} although a calculation using the values given by Pauling gives a resonance energy of 28 kcal.mole^{-1} for pyridine and 16 kcal.mole^{-1} for pyrazine.

On the other hand it is apparent, either that the importance of identical Kekulé-structures for the stability of the aromatic structure in the present case is far less than is generally accepted, or that at least one of Cottrell's bond energy values is in error. From what has been said the second explanation seems to be most probable, particularly as some of the bond energies involving nitrogen are based on very scanty or old experimental data. The E_{C-N}-value given by Cottrell is 72.8 which is an average value for a number of amines, the spread being as much as $\pm$ 3 kcal.mole^{-1}. Recently, Skinner et al.[16] reported heat of combustion values for n-butylamine and sec.-butylamine. From their results E_{C-N} is calculated to be, on the average, 70 kcal.mole^{-1}. Using this value, the resonance energies become 27, 14, 14, and 12 for pyridine, pyrazine, pyrimidine, and pyridazine, respectively. Still, the situation does not seem satisfactory and it might well be that the bond energies necessary for the calculations must be taken from a comparison material containing the structural element C—N=C (Schiff's bases).

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