377. *Heats of Formation and Bond Energies. Part X.** 1,2,5,6-*Tetrahydropyridine, Piperidine, and Piperazine.*

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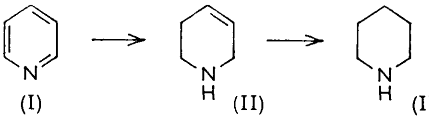
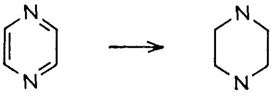
The heats of combustion of the compounds mentioned in the title have been measured. These data have been used to calculate the following ΔH_f° values: 1,2,5,6-tetrahydropyridine (liq.) = $+8{\cdot}00 \pm 0{\cdot}54$; piperidine (liq.) = $-21{\cdot}06 \pm 0{\cdot}54$; piperazine (cryst.) = $-10{\cdot}90 \pm 0{\cdot}38$ kcal./mole. From these the heats of hydrogenation and resonance energies of pyridine and of pyrazine have been obtained.

The resonance energy of pyridine (I) can be determined by comparing its heat of hydrogenation, $\Delta H(\text{I} \longrightarrow \text{III})$, to piperidine (III) with the sum of the heat of hydrogenation, $\Delta H(\text{IV} \longrightarrow \text{V})$, of *N*-n-butylisobutyraldimine (IV) to n-butylisobutylamine (V) and twice the heat of hydrogenation, $\Delta H(\text{VI} \longrightarrow \text{VII})$, of cyclohexene to cyclohexane. Information about the relative strain energies of 1,2,5,6-tetrahydropyridine (II) and piperidine can be obtained by comparing the heat of hydrogenation, $\Delta H(\text{II} \longrightarrow \text{III})$, of 1,2,5,6-tetrahydropyridine to piperidine with the value $\Delta H(\text{VI} \longrightarrow \text{VII})$. The resonance energy of pyrazine (VIII) may be established by comparing its heat of hydrogenation, $\Delta H(\text{VIII} \longrightarrow \text{IX})$, to piperazine (IX) with the sum $2\Delta H(\text{IV} \longrightarrow \text{V}) + \Delta H(\text{VI} \longrightarrow \text{VII})$.



(I) (II) (III)

$Bu^nN = CHPr^i \longrightarrow Bu^n{\cdot}Bu^iNH$
(IV) (V)



(VIII) (IX)

These heats of hydrogenation can be calculated from the heats of formation of the compounds. Accurate values are available for the heats of formation of pyridine,[1]

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* Part IX, *J.*, 1963, 1978.

[1] (*a*) Cox, Challoner, and Meetham, *J.*, 1954, 265; (*b*) McCullough, Douslin, Messerly, Hossenlop, Kincheloe, and Waddington, *J. Amer. Chem. Soc.*, 1957, **79**, 4289.

N-n-butylisobutyraldimine,[2] n-butylisobutylamine,[2] and pyrazine.[3] The heat of gas-phase hydrogenation of cyclohexene to cyclohexane has been measured directly.[4] The heat of combustion of piperidine was measured by Delépine[5] in 1898, and the data reinterpreted by Kharasch,[6] but it seemed advisable to redetermine it. The heats of combustion of 1,2,5,6-tetrahydropyridine and of piperazine are also reported in this paper.

EXPERIMENTAL

Compounds.—1,2,5,6-Tetrahydropyridine (L. Light and Co. Ltd.), piperidine (Robinson Bros. Ltd., " pure grade "), and piperazine (Eastman Kodak. Ltd., " 99% grade ") were distilled through a 36 in. Fenske column. They had b. p. 116·8°/758 mm., 105·8°/745 mm., and 147·0°/758 mm., respectively. Davies and McGee[7] give b. p. 117·4°/771 mm. and 117·0°/757 mm. for 1,2,5,6-tetrahydropyridine. Timmermans[8] gives b. p. 106·40°/760 mm., and dT/dp (10 mm.) = 0·44 for piperidine. Heilbron and Bunbury[9] give m. p. 104° and b. p. 140° for piperazine. 1,2,5,6-Tetrahydropyridine and piperidine had n_{25}^{D} 1·4774 and 1·4499, respectively. The solid piperazine was zone-refined, a Baird and Tatlock semimicro zone-melting apparatus being used. After eight passes, brown impurity no longer accumulated at the bottom of the tube. The sample had m. p. 105°. The three compounds appeared to be pure when analysed with a Perkin-Elmer fractometer and a di-n-decyl phthalate column. Likely impurities, pyridine, piperidine, 1,2,5,6-tetrahydropyridine, and picoline could be detected in concentrations of less than 0·1%. It seems reasonable to conclude that the compounds were at least 99·9% pure.

Combustion Calorimetry.—Combustions were made in a twin-valve bomb (the Parr Instrument Co., Moline, Illinois, U.S.A.) which, together with the subsidiary apparatus, has been described previously.[10] The liquid tetrahydropyridine and piperidine were sealed in glass ampoules, and the solid piperazine, pressed into pellets, was sealed in Melinex bags. All combustions were initiated by a platinum wire and cotton-thread fuse. An additional fuse of hydrocarbon oil was added in the combustion of the tetrahydropyridine and piperidine. The bomb was charged with water (1 ml.) and with oxygen at an initial pressure of 30 atm. Each sample was fired at 25°.

Analysis.—After each combustion the gases in the bomb were analysed for carbon dioxide to an accuracy of ±0·02%. The washings were titrated with 0·1N-sodium hydroxide to determine nitric acid. No carbon was found in the bomb after any of the combustions for which results are reported here.

Units and Auxiliary Quantities.—The heats of combustion are given in units of the thermochemical calorie, 1 cal. = 4·1840 abs. J. The atomic weights used are those recommended by the International Union in 1961, as listed by Wichers.[11] The energy equivalent of the calorimeter was determined according to the method of Prosen,[12] by the combustion of a sample of benzoic acid (B.D.H. Thermochemical Standard, batch no. 760161) having $-\Delta U_b$ (the heat liberated in the actual bomb combustion reaction) $=6319{\cdot}1 \pm 0{\cdot}7$ ($\pm 0{\cdot}012\%$) cal./g. The heats evolved in ancillary processes were taken to have the values given previously.[2]

Results.—The results of the combustions are given in Tables 1—3, in which some of the symbols and their arrangement differ from those in earlier Parts, to conform to recent recommendations about the publication of thermochemical data,[13] and to indicate more clearly the

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[2] Bedford, Edmondson, and Mortimer, *J.*, 1962, 2927.

[3] Tjebbes, *Acta Chem. Scand.*, 1962, **10**, 916.

[4] Dolliver, Gresham, and Kistiakowsky, *J. Amer. Chem. Soc.*, 1937, **59**, 831.

[5] Delépine, *Compt. rend.*, 1898, **126**, 964.

[6] Kharasch, *Bur. Stand. J. Res.*, 1929, **2**, 359.

[7] Davies and McGee, *J.*, 1950, 678.

[8] Timmermans, " Physico-chemical Constants of Pure Organic Compounds," Elsevier, Brussels, 1950.

[9] Heilbron and Bunbury, " Dictionary of Organic Compounds," Eyre and Spottiswoode, London, 1946.

[10] Fletcher, Mortimer, and Springall, *J.*, 1959, 580.

[11] Wichers, *Nature*, 1962, **194**, 621.

[12] Prosen, " Experimental Thermochemistry," Vol. 1, ed. Rossini, Interscience, New York, 1956, Chap. 6.

[13] " Resolution on Publication of Calorimetric and Thermodynamic Data," Bulletin of Chemical Thermodynamics, I.U.P.A.C., No. 4, 1961.

TABLE 1.

1,2,5,6-Tetrahydropyridine (M, 83·134).

Experiment:	1	2	3	4	5
Wt. of sample (g.) * ...	0·742315	0·633102	0·970176	0·709886	0·758053
m_i (g.)	0·002495	0·002419	0·002466	0·002279	0·002220
m_o (g.)	0·033569	0·060490	0·029490	0·041194	0·019211
m_{CO_2} obs (g.)	2·07436	1·86470	2·65766	2·01327	2·06943
CO_2 obs′ : calc′ (%) ...	99·96	99·62	99·70	100·01	99·90
ΔR_c (ohm)	0·18401	0·16538	0·23594	0·17850	0·18364
q_i (cal.)	9·68	9·39	9·45	8·84	8·61
q_n (cal.)	12·83	10·58	15·14	11·09	11·78
q_o (cal.)	368·72	664·41	323·91	452·47	211·01
q_w (cal.)	3·06	2·61	4·27	2·90	3·09
E_c (cal./ohm)	10·79	9·35	14·02	10·36	10·92
$-\Delta U_c°$ (kcal./mole) ...	784·31	785·45	784·67	784·39	784·40

Mean $-\Delta U_c° = 784·64$ kcal./mole (standard deviation of mean $\pm 0·21$ kcal./mole).

* All weights *in vacuo*; d^{25}, 0·903 g./ml. $E_s = 40175·77$ cal./ohm; $\bar{s}E = \pm 0·022\%$; $\bar{s}\Delta U_c° = \pm 0·027\%$; $\bar{s} = \pm 0·035\%$; $\Delta n\boldsymbol{R}T = -1·04$ kcal./mole; $-\Delta H_c° = 785·68 \pm 0·54$ kcal./mole.

TABLE 2.

Piperidine (M, 85·150).

Experiment:	1	2	3	4	5
Wt. of sample (g.) * ...	0·640888	0·680541	0·692712	0·751636	0·881022
m_i (g.)	0·002589	0·002440	0·002185	0·002450	0·002015
m (g.)	0·038658	0·045342	0·036538	0·037998	0·030390
m_{CO_2} obs (g.)	1·77757	1·90300	1·90416	2·06065	2·36962
CO_2 obs′ : calc′ (%) ...	99·69	99·82	99·71	99·69	99·71
ΔR_c (ohm)	0·16503	0·17641	0·17682	0·19122	0·22014
q_i (cal.)	10·05	9·47	8·48	9·50	7·82
q_n (cal.)	11·05	10·22	12·01	10·50	10·50
q_o (cal.)	424·61	498·03	401·33	417·36	333·80
q_w (cal.)	1·99	2·06	2·13	2·36	3·05
E_c (cal./ohm)	11·41	11·08	11·22	12·17	14·19
$-\Delta U_c°$ (kcal./mole) ...	824·35	823·47	823·74	823·30	823·15

Mean $-\Delta U_c° = 823·60$ kcal./mole (standard deviation of mean $\pm 0·19$ kcal./mole).

* d_{25}, 0·8567 g./ml.[8] $E_s = 40175·77$ cal./ohm; $\bar{s}E = \pm 0·022\%$; $\bar{s}\Delta U_c° = \pm 0·022\%$; $\bar{s} = \pm 0·034\%$; $\Delta n\boldsymbol{R}T = -1·34$ kcal./mole; $-\Delta H_c° = 824·94 \pm 0·56$ kcal./mole.

TABLE 3.

Piperazine (M, 86·138).

Experiment:	1	2	3	4	5
Wt. of sample (g.) * ...	0·476100	0·598962	0·539831	0·592775	0·530539
m_i (g.)	0·002765	0·002550	0·002780	0·002482	0·002350
m_m (g.)	0·027560	0·046348	0·040217	0·041947	0·035620
m_{CO_2} obs (g.)	1·039317	1·33437	1·19720	1·30838	1·16713
CO_2 obs′ : calc′ (%) ...	99·87	100·00	99·76	99·74	99·73
ΔR_c (ohm)	0·10132	0·12916	0·11599	0·12693	0·11331
q_i (cal.)	10·73	9·90	10·79	9·63	9·12
q_n (cal.)	12·01	16·16	13·26	13·26	12·15
q_m (cal.)	151·13	254·17	220·54	230·03	195·33
q_w (cal.)	1·08	1·26	1·16	1·34	1·06
E_c (cal./ohm)	6·94	8·77	7·90	8·66	7·66
$-\Delta U_c°$ (kcal./mole) ...	705·85	705·93	706·22	706·09	705·82

Mean $-\Delta U_c° = 705·99$ kcal./mole (standard deviation of mean $\pm 0·02$ kcal./mole).

* d_{25}, 1·26 g./ml. $E_s = 40175·77$ cal./ohm; $\bar{s}E = \pm 0·022\%$; $\bar{s}\Delta U_c° = \pm 0·003\%$; $\bar{s} = \pm 0·027\%$; $\Delta n\boldsymbol{R}T = -0·89$ kcal./mole; $-\Delta H_c° = 706·88 \pm 0·38$ kcal./mole.

steps in the evaluation. The meanings of the symbols and the method of calculation have been given elsewhere.[14] Two additional symbols are used: m_o, the mass of oil; q_o, the heat of combustion of the oil. The uncertainty associated with the value of $\Delta H_c°$ is the overall uncertainty interval, which is twice the standard deviation of the mean, $2\bar{s}$.

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[14] Bedford, Carey, Millar, Mortimer, and Springall, *J.*, 1962, 3895.

The combustions refer to the reactions:

$$C_5H_9N\ (\text{liq.}) + 7{\cdot}25\ O_2\ (g) \longrightarrow 5CO_2\ (g) + 4{\cdot}5H_2O\ (\text{liq.}) + 0{\cdot}5N_2\ (g)$$
$$C_5H_{11}N\ (\text{liq.}) + 7{\cdot}75\ O_2\ (g) \longrightarrow 5CO_2\ (g) + 5{\cdot}5H_2O\ (\text{liq.}) + 0{\cdot}5N_2\ (g)$$
$$C_4H_{10}N_2\ (\text{cryst.}) + 6{\cdot}5\ O_2\ (g) \longrightarrow 4CO_2\ (g) + 5H_2O\ (\text{liq.}) + N_2\ (g)$$

From the ΔH_f° values at 25°, corrected to the 1961 atomic weights: H_2O(liq.), −68·3149 ± 0·0096; and CO_2(g), −94·0517 ± 0·0108 kcal./mole,[15] we calculated the ΔH_f° values at 25°· 1,2,5,6-tetrahydropyridine (liq.), +8·00 ± 0·54; piperidine (liq.), −21·06 ± 0·56; and piperazine (cryst.), −10·90 ± 0·38 kcal./mole.

DISCUSSION

The heat of combustion of liquid piperidine, measured by Delépine,[5] was recalculated by Kharasch [6] as ΔH_c° = −826·6 kcal./mole. McCullough and his co-workers [16] have recently obtained the value −825·29 ± 0·11 kcal./mole, based on a molecular weight of 85·146. The value reported here is −824·94 ± 0·56 kcal./mole. This leads to the value ΔH_f°(liq.) = −21·06 ± 0·56 kcal./mole. Incorporating the latent heat of vaporisation [16] of 9·39 ± 0·05 kcal./mole, we obtain the value ΔH_f°(g) = −11·67 ± 0·61 kcal./mole.

The heat of formation of gaseous cyclohexane is ΔH_f°(g) = −29·43 kcal./mole,[17] so that replacement of a CH_2 group in cyclohexane by an NH group to give piperidine makes the heat of formation, in the gas phase, more positive by 17·76 ± 0·61 kcal./mole. This is close to the difference of 18·0 ± 0·4 kcal./mole between the heats of formation of gaseous diethylamine (−17·0 ± 0·4 kcal./mole [18]) and of gaseous n-pentane (−35·04 ± 0·04 kcal./mole [17]).

The heat of hydrogenation, $\Delta H(\text{II} \longrightarrow \text{III})$, in the liquid phase of 1,2,5,6-tetrahydropyridine to piperidine is calculated from the heats of formation of the two compounds as −29·1 ± 1·1 kcal./mole. It is unlikely that the heat of hydrogenation in the gas phase will differ from this value by more than ±0·5 kcal./mole. Within the experimental error, this heat change is the same as the heat of gas-phase hydrogenation of cyclohexene to cyclohexane, $\Delta H(\text{VI} \longrightarrow \text{VII})$ = −28·59 ± 0·01 kcal./mole.[4] This suggests that the difference between the strain energies of 1,2,5,6-tetrahydropyridine and piperidine is the same as the difference between the strain energies of cyclohexene and cyclohexane, which is small.

Taking the heat of formation of gaseous pyridine as ΔH_f°(g) = +33·63 ± 0·38 kcal./mole,[1a] the heat of hydrogenation to piperidine, $\Delta H(\text{I} \longrightarrow \text{III})$, in the gas phase, is calculated as −45·30 ± 0·94 kcal./mole. This may be compared with a value of −48·3 kcal./mole, at 127—277°, obtained from equilibrium studies by Hales and Herington.[19] Unfortunately, heat capacity data for gaseous piperidine are insufficient to derive an accurate value at 25°. Our calculated heat of hydrogenation is 31·9 ± 2·0 kcal./mole less than the sum, −77·18 ± 1·02 kcal./mole, of the heat of gas-phase hydrogenation of *N*-n-butylisobutyraldimine to n-butylisobutylamine, $\Delta H(\text{IV} \longrightarrow \text{V})$ = −20·0 ± 1·0 kcal./mole,[2] and twice the heat of gas-phase hydrogenation of cyclohexene to cyclohexane, $\Delta H(\text{VI} \longrightarrow \text{VII})$ = −28·59 ± 0·01 kcal./mole.[4] The difference of 31·9 ± 2·0 kcal./mole is taken to be the resonance energy of pyridine.

Taking the heat of formation of pyrazine given by Tjebbes,[3] ΔH_f° (cryst.) = +33·41 ± 0·28 kcal./mole, and our value for the heat of formation of piperazine, we calculate the heat of hydrogenation, in the solid phase, of pyrazine to piperazine as $\Delta H(\text{VIII} \longrightarrow \text{IX})$ = −44·3 ± 0·7 kcal./mole. The heat of hydrogenation in the gas phase is unlikely to differ by more than ±0·5 kcal./mole. This heat of hydrogenation is 24·3 ± 2·7 kcal./mole less

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[15] Wagman, Kilpatrick, Taylor, Pitzer, and Rossini, *J. Res. Nat. Bur. Stand.*, 1945, **34**, 143.

[16] McCullough, U.S. Bureau of Mines, Bartlesville, Oklahoma, U.S.A., personal communications.

[17] American Petroleum Institute Research Project 44, Carnegie Press, Pittsburg, Pa., 1952.

[18] Prosen, National Bureau of Standards, Washington, D.C., U.S.A., personal communication.

[19] Hales and Herington, *Trans. Faraday Soc.*, 1957, **53**, 616.

than the value $2\Delta H(\text{IV} \longrightarrow \text{V}) + \Delta H(\text{VI} \longrightarrow \text{VII}) = -68{\cdot}58 \pm 2{\cdot}01$ kcal./mole. The difference of 24·3 ± 2·7 kcal./mole is taken to be the resonance energy of pyrazine.

From these values it appears that resonance energies decrease along the series benzene (36 kcal./mole [20]), pyridine (32 kcal./mole), and pyrazine (24 kcal./mole).

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[20] Pauling, " The Nature of the Chemical Bond," 3rd edn., Cornell University Press, 1960, p. 193.