The Heats of Combustion of Pyridine and Certain of its Derivatives.

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Precise measurements have been made, by means of a bomb calorimeter, of the heats of combustion of very pure samples of pyridine, the three picolines, and 2 : 5- and 2 : 6-lutidine. The products of combustion were analysed quantitatively, the heats of combustion per mole being calculated from the amount of carbon dioxide formed in the reaction.

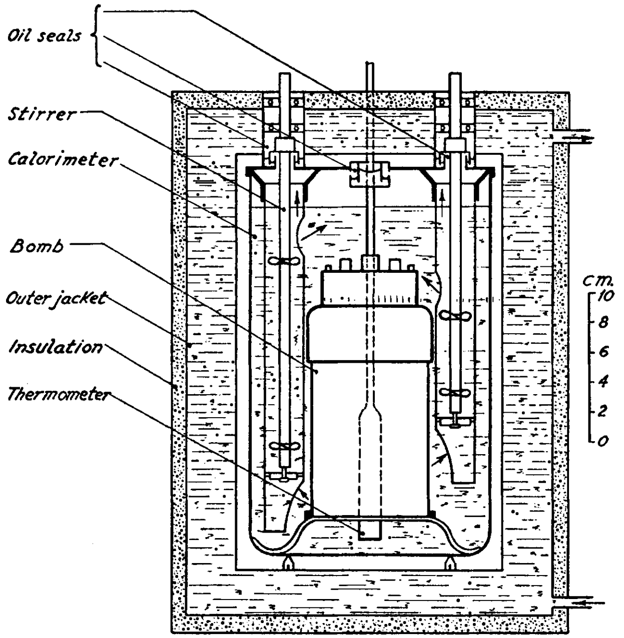
DURING the past two decades, precise measurements have been made of the heats of combustion of a large number of organic compounds, notably hydrocarbons; but such data are lacking for many classes of oxygen- and nitrogen-containing compounds, such as pyridine bases, several of which now have important commercial applications. Although several measurements have been made of the thermochemical properties (including the heat of combustion) of pyridine itself, there is little reliable information on its alkyl derivatives; this is probably due to the difficulty of freeing the pyridine bases from congeners or water. However, the isolation and characterisation of the coal-tar bases is being intensively studied at the Chemical Research Laboratory, and as part of this programme we have measured the heats of combustion at 25° of pyridine, the three picolines, and 2 : 5- and 2 : 6-lutidine. It is hoped eventually to determine the standard entropies of these compounds, and with the aid of the enthalpies of formation from the present work to calculate their free energies of formation.

Considerable difficulty was experienced in freeing the bases from traces of water (cf. Coulson, Hales, and Herington, *J.*, 1951, 2125) and in sealing them in ampoules without ingress of moisture. For this reason it was decided to analyse the combustion products and to calculate the heats of combustion per mole from the amount of carbon dioxide formed rather than from the amount of liquid burnt.

EXPERIMENTAL

Materials.—The pyridine bases were prepared at the Chemical Research Laboratory by methods to be described elsewhere. The purities, in moles %, were determined by the freezing-point method (Herington and Handley, *J.*, 1950, 199) to be as follows: pyridine, 99·85 ± 0·07; α-picoline, 99·93 ± 0·04; β-picoline, 99·97 ± 0·02; γ-picoline, 99·91 ± 0·05; 2 : 5-lutidine, 99·85 ± 0·07; 2 : 6-lutidine, 99·80 ± 0·10. The chief residual impurity was water. Traces of related pyridine bases were probably present but hydrocarbons were absent. The sulphur content of all samples used was less than 10 p.p.m. The liquids were sealed, without being weighed, in glass ampoules of average mass 0·2 g. (*ca.* 0·13 g. without the capillary). The ampoules, of the type described by Richards and Barry (*J. Amer. Chem. Soc.*, 1915, **37**, 993), were blown from soda-glass tubing in a simple mould and had an approximately constant internal volume of 0·85 c.c., equivalent to *ca.* 0·8 g. of liquid; the ampoules were filled as completely as possible, only a small bubble of air being left in the capillary side-arm. It was found advantageous to anneal the ampoules after their removal from the mould in order that, when filled and sealed, they should better withstand the 30 atm. pressure to which they were subjected in the bomb; ampoules which had not been annealed sometimes shattered when subjected to pressure (cf. Aston, Rock, and Isserow, *J. Amer. Chem. Soc.*, 1952, **74**, 2484).

The Bomb Calorimeter.—Two steel bombs, with separate inlet and outlet valves, were used; their internal volumes were 0·277 l. and 0·297 l. severally. Each contained a rubber O-ring and a fibre bush for the insulated electrode, but these combustible materials were shielded from direct radiation of the flame and suffered no observable change during an experiment.



The ampoule was placed at the bottom of a platinum crucible (2·5 cm. in diam. and 1·5 cm. deep) supported in the middle of the bomb. Above it, about 2·4 cm. of 35 S.W.G iron wire (previously weighed) was held by platinum leads 0·5 mm. in diameter which were attached to two electrodes. 1 G. of distilled water was placed in the bottom of the bomb. Five times, oxygen at 5 atm. pressure was admitted to the bomb and released to the air; a trial experiment had shown that 0·95 g. of water now remained in the bomb. The bomb was finally filled with oxygen to 30·6 atm. This oxygen had been purified by passage, at 100 atm. pressure, over copper oxide at 500° then over ascarite in a steel apparatus similar to that described by Prosen and Rossini (*J. Res. Nat. Bur. Stand.*, 1941, **27**, 289). By closing for about one second a tapping key which connected 6 v across the iron wire, the ampoule was opened and the liquid ignited. The electrical energy of ignition was 0·5—0·7 J. On one occasion the residue from the burning of the iron wire was examined by *X*-ray diffraction; it was found to consist entirely of α-Fe_2O_3.

The calorimeter is shown simplified in the Figure. The two stirrers, propellers in tubes, rotating at constant speed, drove the water turbulently throughout the calorimeter. The upper bearings of the stirrers were in thermal contact with the outer jacket, each stirrer shaft passing out of the lid through a thin copper–nickel connector and an oil seal, half filled with clock oil. A third oil seal was attached to the centre of the lid. The dimensions of the seals were such that the materials inside the calorimeter could expand without the escape of air. The evaporation of water from the calorimeter was thus completely prevented. A 10Ω heater of manganin wire wound on mica, in a copper sheath filled with silicone oil, was permanently attached to the lid of the calorimeter, the heating coil being well immersed in the water. The lid was dried and weighed before each experiment to check that there had been no loss of oil. A small manometer could be fitted to the lid to test whether the calorimeter was air-tight. The main parts of the calorimeter and lid were of rhodium-plated brass, 1·6 mm. thick.

After the bomb had been prepared and put in position, the calorimeter was filled with distilled water until the air space at the top was about 100 c.c. (0·6 cm. × 180 cm.^{2}). The mass of the calorimeter including the lid, but with rubber bungs in the thermometer holes, was adjusted by adding water to a total of 10,340 g. (bomb I) or 10,440 g. (bomb II); weighings were reproducible to $\pm 0{\cdot}005$ g.

A double-walled jacket, 2·5 cm. thick and rhodium-plated on the inside, completely enclosed the calorimeter with an air gap of 1 cm. between the two vessels. Internal partitions in the jacket made a labyrinth through which water from a constant-temperature bath was pumped. During an experiment the temperature of the jacket, as measured by multiple thermo-junctions immersed in the water, remained steady to within $\pm 0{\cdot}002°$. The jacket was enclosed by thermal insulation of low heat capacity, and the whole assembly was kept in a room the temperature of which was controlled at 22° ± 0·1°.

Two thermometers were immersed in the calorimeter. The first, a platinum resistance (Gittings, *J. Sci. Instr.*, 1951, **28**, 238), was used in energy-equivalent experiments to measure the initial and final temperatures and in calibrating the second thermometer, of multiple thermo-junctions, which was used in combustion experiments and in following the rise of temperature in electrical-heating experiments. The second thermometer comprised 15 copper–constantan junctions in a silver sheath, the cold junctions being immersed in pure melting ice. Its sensitivity was approximately 600 μv/deg. c, and the e.m.f. was measured with a Diesselhorst potentiometer to the nearest 0·1 μv. The working range of the calorimeter was 23—25° with the outer jacket at 24°. Its energy equivalent in this range, in closely repeated conditions, was determined by dissipating an accurately measured amount of electrical energy in the manganin heating coil and found to be 17,202 ± 3 (bomb I) or 17,218 ± 3 (bomb II) absolute joules per deg. c. In electrical-heating experiments the platinum thermometer was used, with a method of correcting the temperature rise for heat transfer, to be described elsewhere as part of a full account of the calorimeter. Observations made at the same time with the second thermometer were corrected by a simpler method (Dickinson, *Bull. Bur. Stand.*, 1915, **11**, 189); a factor was then found for converting the rise in e.m.f. to the rise (°c) observed with the platinum thermometer.

Units and Auxiliary Quantities.—The energy equivalent of the calorimeter, and hence the heats of combustion, were measured according to international agreement in joules (Griffiths, *Proc. Inst. Mech. Eng.*, 1951, **164**, 215). Conversion to "thermochemical" calories was made by the relation : 1 cal. ≡ 4·1840 abs. joules. Weights calibrated at N.P.L. were used, and molecular weights were calculated from the 1951 International Table of Atomic Weights. The heat of formation of 0·7N-nitric acid (the average concentration of nitric acid in the bomb liquid) from nitrogen, oxygen, and liquid water was taken as −58·6 kJ/mole. The heat of combustion of iron to ferric oxide was assumed to be −6·7 J/mg. The heats of formation of water (liq.) and carbon dioxide (gas) were taken to be −285·840 and −393·513 kJ/mole respectively; all these heat values were obtained from N.B.S. Circular 500.

The Standard-state Correction.—It has long been customary in precise bomb calorimetry to attempt to convert the heat measurement actually made ($n\Delta U_B$) to the more useful quantity $\Delta U°_C$, which represents the change in energy (at constant volume) for a "pure" combustion occurring isothermally at 25° with all participants in their standard states. In the case of the combustion of a compound $C_aH_bO_cN_d$ the "pure" reaction is normally considered to be : $C_aH_bO_cN_d$ (liq. under 1 atm.) $+ \frac{1}{4}(4a + b - 2c)O_2$ (gas, at 1 atm.) $\longrightarrow a CO_2$ (gas, at 1 atm.) $+ \frac{1}{2}bH_2O$ (liq.,under 1 atm.) $+ \frac{1}{2}dN_2$ (gas, at 1 atm.). Washburn (*J. Res. Nat. Bur. Stand.*, 1933, **10**, 525) gave an expression for making the correction from $n\Delta U_B$ to $n\Delta U°_C$ (the "standard state" or "Washburn" correction) for the combustion of a compound $C_aH_bO_c$. Since no comparable expression for nitrogen-containing compounds appears to have been published, it was thought worth while to calculate the standard state correction for combustion of a compound $C_aH_bO_cN_d$. The general method of calculation followed closely that of Washburn (*loc. cit.*) and need not therefore be repeated. The treatment differed, however, in the following particulars : (i) A mean temperature of 25° was assumed instead of 20°. (ii) The presence of nitrogen in the gas phase after combustion was allowed for in calculating Δp and x (see below for definition of symbols). The expression for the dependence of the internal energy of the nitrogen on its partial pressure was calculated from the data for air given by Rossini and Frandsen (*ibid.*, 1932, **9**, 733). (iii) The presence of nitric acid in the aqueous phase after combustion was allowed for in the calculation of the water vapour pressure (Klemenc and Nagel, *Z. anorg. Chem.*, 1926, **155**, 257), the solubility of carbon dioxide in the aqueous phase, and the energy of vaporisation of carbon dioxide from the aqueous phase. Appropriate data were taken from " International Critical Tables " and from Mellor, " A Comprehensive Treatise on Inorganic and Theoretical Chemistry " (Longmans, London, 1947, Vol. VI, pp. 47—53).

The total correction in joules to be added to $n\Delta U_B$ to give $n\Delta U^{\circ}_C$ was found to be as follows :

$$-6{\cdot}55an\left\{-\Delta p\left(\frac{1}{x}+\frac{h}{x}\right)-\frac{hp_1}{x}+(p_1-1)\left[\frac{(b-2c)}{4a}+\frac{(4\phi+2\delta)}{4an}\right]-\frac{2{\cdot}45(m_w+9bn)}{V}+\frac{0{\cdot}027\,V\Delta p}{an}+6{\cdot}69\right\}$$

where a, b, c, and d are the subscripts in the molecular formula of the compound ($C_aH_bO_cN_d$) ; n is the number of moles burnt ; x is the mole-fraction of CO_2 in the gas phase after combustion ; Δp is the change in total pressure brought about by the combustion, calculated as if the combustion had taken place isothermally at 25° ; h is defined by the expression $h = 1{\cdot}7x(1 + x)$; p_1 is the pressure in the bomb (at 25°) before combustion ; δ is the number of moles of nitric acid formed ; ϕ is the number of moles of oxygen giving rise to nitric acid plus ferric oxide ; m_w is the mass of water in the bomb before combustion ; and V is the internal volume of the bomb in litres.

It will be noted that d does not appear in the above expression. This is because the only term containing it explicitly was found to be negligible. However, d must be taken into account when x is calculated from the expression :

$$x = \frac{0{\cdot}996an}{n_{O_2}-\dfrac{(b-2c)n}{4}-\phi+\dfrac{(dn-\delta)}{2}}$$

In a series of combustions of any one compound, a, b, c, and d are constants and it is normal practice to keep p_1, m_w, and V constant also. If the mass of material burnt is kept the same (within $\pm 10\%$) during a series of experiments, x, ϕ, δ, and Δp can likewise be considered as constants. The standard-state correction then reduces to the form : Bn, where B is a constant which can be calculated by substitution of appropriate values into the expressions given above.

Analytical Methods.—The number of moles of compound burnt was calculated from the mass of carbon dioxide formed. For the determination of the latter and of carbon monoxide, a glass absorption train similar to that described by Prosen and Rossini (*loc. cit.*) was used, the bomb being connected to the train by B7 metal joints. Carbon dioxide in the combustion product was absorbed by soda–asbestos packed in U-tubes which were fitted with taps and standard taper joints. The U-tubes were flushed out with hydrogen for 1 hr. before weighings were made, and the bomb was flushed through with oxygen for 2 hr. after the compressed gas had been released. The weighing technique and the method of correcting the weighings to a vacuum basis were based on the work of Rossini (*J. Res. Nat. Bur. Stand.*, 1931, **6**, 1, 37). It was found in " blank " experiments that the U-absorbers remained constant in weight to within ±0·0001 g. In the great majority of experiments, carbon monoxide in the combustion product amounted to less than 0·0002 g. In about half of the experiments no soot was formed but in the remainder small patches of soot, of average mass 0·0002 g. (corresponding to *ca.* 0·03% of the total carbon), were found in the platinum crucible.

The solution of nitric acid remaining in the bomb was rinsed out with distilled water and titrated with 0·1N-sodium hydroxide, a pH meter and glass electrode being used to determine the end-point. It was confirmed in one experiment in which the bomb gases were passed through a scrubber that no significant amount of nitric acid is lost from the bomb during the release of the compressed gas. The neutralised nitric acid solutions from several combustions of 2 : 6-lutidine were examined by ultra-violet spectroscopy ; although traces of unburnt lutidine (corresponding to *ca.* 0·03% of the lutidine burnt) could be detected, no other compounds having absorption in the ultra-violet were present. On a number of occasions the bomb liquid was analysed for nitrite, cyanide, and ammonia and the bomb gas was analysed for nitrogen dioxide. In no case did any of these entities account for more than 0·1% of the nitrogen present.

Results.—In Table 1, $-n\Delta U_B$ is the measured energy change for the reaction occurring in the bomb, and $-q_{HNO_3}$ and $-q_{Fe_2O_3}$ are corrections to be subtracted from $-n\Delta U_B$ to take account of the formation of nitric acid and ferric oxide respectively. The standard-state correction, $-q_{s.s.}$, is also to be subtracted from $-n\Delta U_B$. From the mean values of ΔU°_C (Table 1) for the six compounds studied, the corresponding values of ΔH°_C and ΔH°_f (respectively the enthalpies of combustion and formation under standard conditions) were calculated; these are set out in Table 2.

TABLE 1. *Heats of combustion of six pyridine bases at 25°.*

Compound	Mass of CO_2 formed (g.)	$10^3 n$	$-n\Delta U_B$ (J)	$-q_{HNO_3}$ (J)	$-q_{Fe_2O_3}$ (J)	$-q_{s.s.}$ (J)	$-\Delta U^\circ_C$ (*k*J/mole)
Pyridine (C_5H_5N) …………	2·2466	10·209	28,559	64	53	16	2784·4
	2·4204	10·999	30,666	66	55	17	2775·5
	2·2140	10·061	28,101	60	51	16	2780·4
	2·3830	10·829	30,298	68	54	17	2785·1
	2·1696	9·860	27,526	59	54	15	2778·6
	2·1691	9·857	27,526	60	54	15	2779·3
α-Picoline (C_6H_7N) ………	2·6292	8·570	29,392	58	53	15	3415·1
	2·4360	9·225	31,642	63	52	16	3415·8
	2·0727	7·849	26,975	66	57	13	3419·4
	2·3006	8·712	29,936	56	55	15	3421·8
	2·2382	8·476	29,071	56	55	15	3415·1
β-Picoline (C_6H_7N) ………	2·1669	8·206	28,260	52	54	14	3429·1
	2·2623	8·567	29,494	54	52	15	3428·6
	2·3034	8·723	30,021	58	55	15	3427·0
	2·0659	7·824	26,913	49	55	13	3424·8
	2·1144	8·007	27,538	53	56	14	3424·0
γ-Picoline (C_6H_7N) ………	2·4436	9·254	31,747	74	51	16	3415·4
	2·3078	8·740	29,977	66	49	15	3415·0
	2·1910	8·297	28,482	57	54	14	3417·6
	2·4304	9·204	31,551	62	54	16	3413·7
	2·3127	8·758	30,028	56	54	15	3414·4
2 : 5-Lutidine (C_7H_9N) …	2·2506	7·305	29,710	50	52	14	4051·2
	2·2756	7·387	30,063	47	50	14	4054·7
	2·2810	7·404	30,145	49	50	14	4056·2
	2·2934	7·444	30,297	50	50	15	4054·7
2 : 6-Lutidine (C_7H_9N) …	2·3689	7·689	31,208	58	53	15	4042·4
	2·3662	7·681	31,225	55	54	15	4049·1
	2·1546	6·994	28,384	48	51	14	4042·2
	2·1933	7·119	28,912	53	51	14	4044·7
	2·2667	7·358	29,935	55	52	14	4051·8
	2·2807	7·403	30,100	55	52	14	4049·6

TABLE 2. *Heats of combustion and formation at 25° of six pyridine bases (kcal./mole).*

	Liquid state			Gaseous state	
Compound	ΔU°_C *	ΔH°_C	ΔH°_f	ΔH°_C †	ΔH°_f †
Pyridine ………………	−664·58 ± 0·36	−665·00	+23·95	−674·68	+33·63
α-Picoline ……………	−816·78 ± 0·31	−817·52	+14·10	−827·80	+24·38
β-Picoline ……………	−819·00 ± 0·24	−819·74	+16·32	−830·58	+27·16
γ-Picoline ……………	−816·25 ± 0·15	−816·99	+13·57	−827·85	+24·43
2 : 5-Lutidine …………	−968·98 ± 0·29	−970·02	+ 4·23	−981·46	+15·67
2 : 6-Lutidine …………	−967·16 ± 0·37	−968·20	+ 2·41	−979·22	+13·43

* This column gives also standard deviations of the mean; they apply also to the corresponding values of ΔH°_C and ΔH°_f for the liquid state. They measure " reproducibility," not " accuracy " which would be affected by systematic errors.

† In the calculation of these quantities the assumption was made that the six compounds behave as ideal gases. If deviation from ideality could be taken into account, each value of $-\Delta H^\circ_C$ and ΔH°_f would probably be reduced by *ca.* 0·5 kcal. but for purposes of intercomparison within this series of compounds, the errors in column * may be taken to apply to corresponding values of ΔH°_C and ΔH°_f for the gaseous state.

DISCUSSION

It is rather difficult to assess the systematic errors that must have occurred in the measurements, but they must include the following: (1) The method of estimating the number of moles of each sample burnt, from the yield of carbon dioxide, was examined for systematic errors by applying it to known masses of benzoic acid (thermochemical standard, from the National Bureau of Standards). In four experiments the ratio of CO_2(found) to CO_2(calc.) was 1·0001, 0·9999, 1·0000, and 0·9997. The average 0·99992 ± 0·00008 was not significantly different from unity and the systematic error was not likely to exceed 0·016%.

(2) Impurities were of the order of 0·1 mole %. They would introduce errors only if they burnt and yielded an amount of heat per mole of carbon dioxide formed different from that of the pure base. The most likely impurities, water and compounds isomeric with the base, would affect $\Delta H°_C$ very slightly indeed.

(3) Incomplete combustion could not have occurred without leaving visible soot or measurable carbon monoxide. From the amounts of these that were found, the maximum error due to incomplete combustion was estimated to be 0·013%; the persistent component of this error would be less.

(4) The calorimeter equivalent, determined electrically under conditions similar to those of combustion experiments, was found with a " reproducibility " error of 0·018%.

(5) The systematic differences between an electrical heating and a combustion are still under investigation. They include differences in the rate at which the temperature of the calorimeter rises, and heat generated in the heater leads in the interspace between calorimeter and outer jacket. Preliminary results indicate that systematic errors from these causes do not exceed the " reproducibility " error of 0·018%.

The systematic errors seem unlikely to add up to more than the average standard error in Table 2, 0·034%. One would then expect that, if independent determinations of the heats of combustion are made, they will fall within three times the standard errors quoted, *i.e.*, within 0·1% of $\Delta H°_C$ in Table 2.

The heat of combustion of liquid pyridine has been measured by Constam and White (*Amer. Chem. J.*, 1903, **29**, 1) and by Delépine (*Compt. rend.*, 1898, **126**, 1794). Their results have been recalculated by Kharasch (*J. Res. Nat. Bur. Stand.*, 1929, **2**, 359) to be —658·5 and —664·8 kcal./mole, respectively; these values can be compared with the values of $\Delta H°_C$ for liquid pyridine given in Table 2. It is seen that the value found in the present work is in good agreement with that of Delépine but in poor agreement with that of Constam and White. The latter workers also measured the heats of combustion of α-, β-, and γ-picoline and of an unspecified lutidine and found values of —815·2, —812·2, —815·8, and —968·0 kcal./mole, respectively (Kharasch *loc. cit.*). The lutidine was probably the 2 : 6-isomer as it was isolated from a γ-picoline fraction of coal-tar origin (cf. Coulson and Jones, *J. Soc. Chem. Ind.*, 1946, **65**, 169). Constam and White's result for lutidine is seen to be in good agreement with the result reported here. The agreement in the case of the picolines is, however, less good, and it seems probable that some of the samples used by Constam and White (notably that of β-picoline) were rather impure, water and congeners being likely contaminants. It is noteworthy that Constam and White employed crystalline derivatives to " purify " their bases. Andon and Cox (*J.*, 1952, 4601) have shown that the sample of β-picoline " purified " in this way by Flaschner (*J.*, 1909, **95**, 668) must in fact have been a mixture containing higher homologues of pyridine.

The heats of formation of the six compounds in the gaseous state, shown in Table 2, were calculated by combining values of $\Delta H°_f$ for the liquid state with latent heats of vaporisation at 25°. In the absence of equation of state data we have assumed that the bases behave as ideal gases. The latent heats were calculated from the very accurate vapour-pressure data of Herington and Martin (*Trans. Faraday Soc.*, 1953, **49**, 154), and although the measurements of these workers did not extend to 25° there is good reason to believe that the calculated latent heats at 25° will not be greatly in error. This belief is supported in the case of pyridine by the reasonable agreement between the value used here (9·68 kcal./mole) and the value (9·48 kcal./mole) obtained by extrapolating Hieber and Woerner's calorimetric measurements (*Z. Elektrochem.*, 1934, **40**, 252) to 25°. From Meulen and Mann's vapour-pressure data (*J. Amer. Chem. Soc.*, 1931, **53**, 451), which cover the range —20° to +120°, and again with the assumption that the base behaves as an ideal gas, a value of 9·85 kcal./mole is obtained.

The increase in $-\Delta H°_C$ (gas) between pyridine and β-picoline, 156 kcal./mole, does not differ significantly from the normal increase associated with a CH_2 group. *E.g.*, Prosen and Rossini (*J. Res. Nat. Bur. Stand.*, 1945, **34**, 263) found a mean increment in $-\Delta H°_C$ (gas) per CH_2 group of 157·4 kcal., in the paraffin series; the increment in the alkylbenzene series is also about 157 kcal. (Klages, *Chem. Ber.*, 1949, **82**, 358). The substitution of a methyl group in the α- or the γ-position of the pyridine ring, however, gives rise to an increase in $-\Delta H°_C$ (gas) of only 153 kcal., while the data for 2 : 5- and 2 : 6-lutidine show that the increase brought about by substituting a methyl group into the α′-position of a picoline is only 151 kcal. It would appear, therefore, that the pyridine ring exerts an appreciable influence on the heats of combustion of methyl groups attached to it at the α- or γ-position.

Pauling ("The Nature of the Chemical Bond," Cornell Univ. Press, New York, 1945, p. 137) has used Constam and White's heat of combustion data to calculate the resonance energy of pyridine. He found a value of 43 kcal./mole, compared with 39 kcal./mole for benzene. If, however, the heat of combustion from the present work is used in conjunction with Pauling's values for heats of atomisation and bond energies, the resonance energy of pyridine is found to be 35 kcal./mole. The compilations by Coates and Sutton (*J.*, 1948, 1187) and Klages (*loc. cit.*) lead to resonance energies of 21—31, and 22 kcal./mole, respectively. It is thus seen that the heat of combustion from the present work apparently leads to a resonance energy of pyridine lower than that of benzene by up to 18 kcal./mole, whereas there is indirect evidence from other sources to suggest that the resonance energies of pyridine and benzene are in fact about the same (Syrkin and Dyatkina, "Structure of Molecules," Butterworths, London, 1950, p. 247; Albert and Willis, *Nature*, 1946, **157**, 341; Pauling and Schomaker, *J. Amer. Chem. Soc.*, 1939, **61**, 1769; Simonetta, *J. Chim. physique*, 1952, **49**, 68). A likely cause of this discrepancy lies in the use of an erroneous value for the bond energy of the C=N group in the calculation of resonance energy. Coates and Sutton (*loc. cit.*) found 96—106 kcal. for this bond-energy term from a study of straight-chain compounds but no values are yet available for the C=N group in a six-membered ring. In view, however, of the lack of agreement as to the best system of bond energies to use in calculation of resonance energies further speculation is pointless.

The standard entropy of pyridine has been determined calorimetrically by Pearce and Bakke (*Proc. Iowa Acad. Sci.*, 1936, **43**, 171) and by Parks, Todd, and Moore (*J. Amer. Chem. Soc.*, 1936, **58**, 398). In addition, Kline and Turkevich (*J. Chem. Phys.*, 1944, **12**, 300) have calculated the entropy of gaseous pyridine at 25° from spectral data. The measurements by Parks, Todd, and Moore (*loc. cit.*), which appear to be reliable, lead to a value of − 65·0 cal./deg.-mole for the entropy of formation of liquid pyridine from its elements at 25°. Combination of this entropy with the enthalpy of formation from Table 2 leads to a value of +43·3 kcal./mole for the free energy of formation of pyridine at 25°.

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