204. *Heats of Combustion. Part II.* The Six Lutidines.*

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The heats of combustion, and hence the heats of formation, of the six isomeric lutidines (dimethylpyridines) have been determined by means of an electrically-calibrated bomb calorimeter. From the results, the heat change for the isomerisation of one liquid lutidine into another can be calculated.

Heats of combustion of the six lutidines were measured. Although the heats of combustion of 2 : 5- and 2 : 6-lutidine were determined a few years ago,[1] it was decided to make further measurements on them because of the desirability of having values for isomers determined under closely standardised conditions. Owing to the hygroscopic nature of pyridine and its homologues, it was preferred in the earlier work [1] to calculate the heat of combustion per mole from the mass of carbon dioxide formed. In the present study, however, the more conventional procedure was used of calculating the heat of combustion per mole from the mass of substance burned.

Experimental

Materials.—Samples of 2 : 3-, 3 : 4-, and 3 : 5-lutidine [2] were synthesised, and samples of 2 : 4-, 2 : 5-, and 2 : 6-lutidine were isolated from coal-tar bases,[3] by Dr. E. A. Coulson and his colleagues. Methods of bringing 2 : 6-lutidine to great purity have been described; [4] methods for purifying the others will be given in due course. The purities of the actual specimens employed (in moles %), as determined cryoscopically [5,6] before the intensive drying described below, were: 2 : 3-, 99·65 ± 0·17; 2 : 4-, 99·80 ± 0·10; 2 : 5-, 99·85 ± 0·07; 2 : 6-, 99·89 ± 0·05; 3 : 4-, 99·88 ± 0·06; and 3 : 5-lutidine, 99·74 ± 0·13.

The above purity measurements were made on samples which had been dried by distillation, but infrared spectroscopy [7] disclosed that water was still present in all the samples; indeed, the water contents, as indicated by quantitative spectroscopic analysis, corresponded within experimental error with the total amounts of impurity found cryoscopically, except for the sample of 3 : 5-lutidine where there appeared to be *ca.* 0·2 mole % of impurity other than water.

To determine heats of combustion per mole to an accuracy of 1 part in 10,000 from the mass of liquid burned, the water contents of the samples should not have exceeded 0·01 wt. % = 0·06 mole %. Earlier experience had shown that intensive drying of pyridine bases by many chemical drying agents is attended by the *formation* of impurities, but it has now been established that calcium hydride, which has been successfully used for drying numerous sulphur compounds,[8] is free from this objection. Moreover, calcium hydride is so effective as a drying

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* The paper by Cox, Challoner, and Meetham, *J.*, 1954, 265, is regarded as Part I.

[1] Cox, Challoner, and Meetham, *J.*, 1954, 265.

[2] Coulson and Ditcham, *J.*, 1957, 356.

[3] Coulson, Hales, Holt, and Ditcham, *J. Appl. Chem.*, 1952, **2**, 71.

[4] Biddiscombe, Coulson, Handley, and Herington, *J.*, 1954, 1957.

[5] Herington, *Analyt. Chim. Acta*, 1957, **16**, 15.

[6] Handley, *ibid.*, p. 115.

[7] Coulson, Hales, and Herington, *J.*, 1951, 2125.

[8] Reports of the American Petroleum Institute's Project 48, communicated by Dr. G. Waddington.

agent that the water content of a lutidine stored over powdered calcium hydride for several days is reduced below 0·01 wt. %.

Filling into Ampoules.—Samples of the lutidines, dried by standing for at least 3 days over calcium hydride, were dispensed into soda-glass ampoules (mass *ca.* 80 mg.) of the pattern described by Guthrie *et al.*[9] by means of a vacuum apparatus similar to that used by them, except that a glass rack was used to support the ampoules during filling. This consisted of two parallel circular glass plates, one vertically above the other and fused at their centres to a long glass rod. The bottom plate rested on glass lugs fused into the wall of the filling vessel. Each ampoule rested on the upper plate with its stalk projecting down through a hole in each plate, and up to six could be filled at once, after which they were sealed in turn by use of a minute hydrogen flame.[9] The stalks were placed in a vacuum desiccator to remove excess of lutidine, and finally each ampoule with its stalk was weighed; weights calibrated at the National Physical Laboratory were used, and conversion to a vacuum basis was made in the usual way.

Calorimetry.—The bomb calorimeter used has been described;[10, 11] of the two bombs available, only that of internal volume 0·297 l. was employed. The energy equivalent of the calorimeter containing this bomb was determined electrically[10, 11] as 17,275·8 ± 0·9 J/deg. for a standard mass of 10,430·00 g.; very small adjustments to the energy equivalent were made to take account of any departures from the standard mass in individual experiments.

Two important changes in the earlier calorimetric technique[1] were made. (i) The ampoule was burst and its contents were ignited by means of a fuse of *ca.* 10 mg. of Polythene, which was itself ignited by connecting a 6 V supply across a short length of platinum wire[10] (0·1 mm. diam.). The Polythene was in the form of thin rings, cut from tubing, which were hung from the platinum wire so that they touched the top of an ampoule lying in the platinum crucible. A flux-meter in the firing circuit indicated the electrical energy of ignition. (ii) All temperatures were measured with the platinum-resistance thermometer.

Analysis of Bomb Products.—The nitric acid formed was determined by titration of the bomb washings with 0·1N-sodium hydroxide solution. Analysis of the bomb gases for carbon dioxide or carbon monoxide was not carried out systematically, although a few checks were made (cf. ref. 1). Earlier experience had indicated that when appreciable amounts of carbon monoxide are present in the bomb gases, patches of soot are invariably to be found in the bomb. Hence, we rejected experiments in which soot was found after combustion (3 out of 41). Experiments in which the characteristic smell of lutidine was detected in the neutralised bomb washings were also rejected (3 further experiments out of 41). Tests showed that 0·1 mg. of a lutidine could thus be unambiguously detected.

Units and Auxiliary Data.—The energy equivalent of the calorimeter was determined electrically in absolute joules; conversion into "thermochemical" calories was made by the definition 1 cal. = 4·1840 J. The 1953 international atomic weights were used.[12] The energy of formation of nitric acid from nitrogen, oxygen, and water was taken as −57·8 kJ/mole.[13] Strictly, this value refers to 0·1N-nitric acid, whereas the *average* concentration of nitric acid in the bomb, after combustion of a lutidine sample with 1 g. of water initially in the bomb, was 0·7N. However, since there was no proof that the concentration of nitric acid in the condensed liquid was uniform throughout the bomb, and since also the energy of dilution of nitric acid from 0·7N to 0·1N is very small (*ca.* −0·16 kJ/mole[14]), we preferred to employ the commonly used value for the energy of formation of nitric acid. The energy of combustion of Polythene was measured in 4 experiments as −46·24 ± 0·05 kJ/g. (−11·05 kcal./g.). The enthalpy of formation of liquid water was taken as −285·840 kJ/mole[14] (−68·3174 kcal./mole) and that of gaseous carbon dioxide as −393·513 kJ/mole[14] (−94·0518 kcal./mole).

Results.—Values of the measured energy changes for the reactions occurring in the bomb are given in Table 1, which also lists the corrections (all to be subtracted numerically from the measured energy change) for the formation of nitric acid, $-q_{\mathrm{HNO_3}}$; for the combustion of Polythene, $-q_{\mathrm{P}}$; for electrical ignition, $-q_{\mathrm{e.i.}}$; and for the conversion to the standard state,

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[9] Guthrie, Scott, Hubbard, Katz, McCullough, Gross, Williamson, and Waddington, *J. Amer. Chem. Soc.*, 1952, **74**, 4662.

[10] Challoner, Gundry, and Meetham, *Phil. Trans.*, 1955, **247**, 553.

[11] Gundry and Meetham, to be published.

[12] *J.*, 1954, 4713.

[13] Rossini, "Experimental Thermochemistry," Interscience, New York, 1956, p. 142.

[14] "Selected Values of Chemical Thermodynamic Properties," National Bureau of Standards Circular 500, Washington, 1952.

$-q_{\mathrm{s.s.}}$; the last correction was calculated by the method previously given.[1] The corrected temperature rises in Table 1 were calculated according to ref. 10. In order to avoid the tedium of making a separate standard-state correction for the Polythene fuse, the empirical formula of the lutidine was weighted to take account of the Polythene employed. The very small correction for the disappearance of reactants and the appearance of products, which Washburn[15] called the "isothermal correction," was made separately from the standard-state correction; after application of this correction the values given in col. 4 of Table 1 were obtained. The final column of Table 1 gives values of the energy change, $-\Delta U_c^\circ$, for the following combustion reaction at 25°: C_7H_9N (liq.) + $37/4O_2 \longrightarrow 7CO_2 + 9/2H_2O$ (liq.) + $\frac{1}{2}N_2$.

TABLE 1.

Compound	Mass (g.)	Temp. rise (corr.) (° C)	Heat evolved (J)	$-q_{\mathrm{HNO_3}}$ (J)	$-q_{\mathrm{p}}$ (J)	$-q_{\mathrm{e.i.}}$ (J)	$-q_{\mathrm{s.s.}}$ (J)	$-\Delta U_c^\circ$ (kJ/mole)
2 : 3-Lutidine	0·96756	2·15315	37210·9	64·6	495·3	0·5	18·8	4056·7
	0·89372	1·99149	34420·5	67·7	508·8	0·5	17·1	4055·5
	1·10340	2·44732	42300·6	86·2	410·0	0·8	21·9	4057·4
	0·86936	1·93607	33459·4	55·1	484·3	0·5	16·6	4055·3
	0·89376	1·98776	34355·3	61·7	461·4	0·7	17·1	4053·9
							Average	4055·8
2 : 4-Lutidine	0·69762	1·55835	26932·4	47·1	490·1	0·6	12·8	4052·1
	0·66033	1·47640	25516·8	51·0	476·2	0·6	12·1	4052·9
	0·75690	1·69133	29231·3	52·8	527·0	0·6	14·2	4053·9
	0·68857	1·53870	26594·3	51·5	488·4	0·6	12·7	4052·3
	0·61762	1·38416	23921·1	50·1	504·5	0·6	11·2	4051·8
	0·75734	1·68802	29172·4	50·6	464·6	0·6	14·1	4052·4
							Average	4052·6
2 : 5-Lutidine	0·52145	1·17260	20266·1	43·7	478·8	0·6	9·3	4055·0
	0·55700	1·25061	21614·3	43·2	478·9	0·5	10·0	4055·5
	0·55968	1·25640	21714·7	45·7	478·9	0·5	10·0	4054·8
	0·56072	1·25738	21732·3	44·2	463·4	0·6	10·0	4053·9
	0·82488	1·84345	31860·9	63·7	554·5	0·7	15·6	4056·2
							Average	4055·1
2 : 6-Lutidine	0·70309	1·56972	27130·1	53·8	473·9	0·6	12·9	4052·1
	0·53846	1·20845	20883·5	45·2	479·2	0·5	9·6	4049·3
	0·65075	1·45382	25123·8	49·0	490·2	0·5	11·9	4046·0
	0·68893	1·53794	26578·6	47·0	478·8	0·7	12·7	4049·9
	0·64512	1·44075	24899·5	48·2	463·4	0·6	11·8	4048·6
	0·84517	1·87623	32429·4	55·6	421·8	0·8	16·2	4048·7
	0·90899	2·02126	34934·7	66·9	498·7	0·6	17·5	4049·2
							Average	4049·1
3 : 4-Lutidine	0·86508	1·92806	33319·9	67·7	487·1	0·6	16·5	4056·2
	0·73064	1·63432	28243·9	48·7	535·8	0·5	13·5	4054·3
	0·85508	1·90657	32950·5	60·0	515·8	0·5	16·3	4054·8
	0·78178	1·74413	30142·1	59·9	497·7	0·6	14·7	4052·7
	0·79351	1·76989	30589·4	63·0	478·9	0·6	14·9	4055·3
	0·85812	1·90644	32949·9	60·0	399·1	0·5	16·3	4054·9
							Average	4054·7
3 : 5-Lutidine	0·72811	1·63002	28172·6	52·8	532·2	0·5	13·5	4057·8
	0·82643	1·84724	31926·7	58·0	543·8	0·6	15·6	4059·3
	0·72679	1·62852	28142·9	54·0	533·5	0·6	13·5	4060·4
	0·77995	1·74702	30192·9	64·4	567·7	0·5	14·7	4059·0
	0·74800	1·66828	28831·9	48·5	437·7	0·5	13·9	4058·4
	0·84777	1·89427	32738·1	59·7	551·1	0·6	16·1	4058·5
							Average	4058·9

DISCUSSION

Mean values of ΔU_c°, ΔH_c°, and ΔH_f° for the liquid state are presented in Table 2 (where all values are given in kcal./mole), together with the standard deviations of the mean. Comparison of these standard errors with those in Table 2 of ref. 1 reveals that the precision of the present work is somewhat the greater, probably due to some or all of the following improvements: (i) only one bomb was used, (ii) temperatures were measured

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[15] Washburn, *J. Res. Nat. Bur. Stand.*, 1933, **10**, 525.

by a platinum-resistance thermometer, (iii) the heat of combustion per mole was calculated directly from the mass of sample taken, (iv) rejection of experiments on suspicion of poor combustion was more rigorous.

TABLE 2.

Lutidine	$\Delta U_c°$	$\Delta H_c°$	$\Delta H_f°$	σ_1 *	σ_2 †	Lutidine	$\Delta U_c°$	$\Delta H_c°$	$\Delta H_f°$	σ_1 *	σ_2 †
2 : 3-	−969·36	−970·40	+4·61	0·14	0·15	2 : 6-	−967·76	−968·80	+3·01	0·17	0·18
2 : 4-	−968·59	−969·63	+3·84	0·08	0·09	3 : 4-	−969·10	−970·14	+4·35	0·11	0·12
2 : 5-	−969·19	−970·23	+4·44	0·10	0·11	3 : 5-	−970·10	−971·14	+5·35	0·09	0·10

* σ_1 is the standard deviation of the mean value of $\Delta U_c°$ *without* considering the standard error of the energy equivalent of the calorimeter; it should be used when making internal comparison within the lutidine series, *e.g.*, for deriving heats of isomerisation. σ_1 also applies to values of $\Delta H_c°$ and $\Delta H_f°$ for purposes of internal comparison.

† σ_2 is the standard deviation of the mean value of $\Delta U_c°$ (or $\Delta H_c°$, or $\Delta H_f°$) when the standard error of the energy equivalent of the calorimeter is considered; it should be used for making comparisons with other work.

The problem of *systematic* errors was discussed earlier[1] under five headings. The first does not apply to the present work, since the heats of combustion per mole are no longer based on the mass of carbon dioxide formed, whilst the issue discussed under the fifth heading, concerning the difference between electrical-heating and combustion experiments, has since been resolved.[10] Of the remaining systematic errors, probably those due to impurities in the samples are alone appreciable.

Values of $\Delta U_c°$ for 2 : 5- and 2 : 6-lutidine were given earlier,[1] and comparison with the present values reveals close agreement for 2 : 5-lutidine but less close agreement for 2 : 6-lutidine; however, the difference between the present and earlier values in the latter instance is not statistically significant, having regard to the known standard errors. The present value is to be preferred, not merely because the reproducibility error is smaller, but also because the systematic errors are thought to be smaller. Values of the heats of formation of all the lutidines in the ideal-gas state cannot yet be given because latent heats of vaporisation at 25° and second virial coefficients are available only for 2 : 6-lutidine,[16] although it is hoped that data for the other lutidines will be available later.

The difference between values of $\Delta H_c°$ for any pair of lutidines corresponds to the heat of isomerisation of one to the other, $\Delta H_i°$, in the liquid state. Thus, the following values were deduced from Table 2:

$\Delta H_i°$ (kcal./mole) for
2 : 6- ⟶ 2 : 4-Lutidine, + 0·84 ± 0·19
2 : 6- ⟶ 3 : 4-Lutidine, + 1·34 ± 0·20
2 : 6- ⟶ 2 : 5-Lutidine, + 1·43 ± 0·20

$\Delta H_i°$ (kcal./mole) for
2 : 6- ⟶ 2 : 3-Lutidine, + 1·60 ± 0·22
2 : 6- ⟶ 3 : 5-Lutidine, + 2·34 ± 0·19

These heats of isomerisation are considerably greater in magnitude than those in the structurally similar xylene series, where $\Delta H_i°$ (liquid state) for *m*- ⟶ *o*-xylene and for *m*- ⟶ *p*-xylene is +0·24[17] to +0·45[18] kcal./mole. Values of $\Delta H_c°$ for the xylenes in the *gas* state are also numerically small (<0·5 kcal./mole), but until latent heats of vaporisation and second virial coefficients are available for all the lutidines it cannot be decided whether the relatively large heats of isomerisation of the lutidines are due to differences in resonance energy or in liquid structure.

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[16] Andon, Cox, Herington, and Martin, *Trans. Faraday Soc.*, 1957, **53**, 1074.
[17] Prosen, Gilmont, and Rossini, *J. Res. Nat. Bur. Stand.*, 1945, **34**, 259, 263.
[18] Coops, Mulder, Dienske, and Smittenberg, *Rec. Trav. chim.*, 1946, **65**, 128.