

568. *Heats of Formation and Bond Energies. Part VI.* n-Butylisobutyraldimine, n-Butylisobutylamine, Pyrazole, and Imidazole.*

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The heats of combustion of the compounds mentioned in the title have been measured. These values are used to calculate the following ΔH_f^0 values; n-butylisobutyraldimine (liq.), -31.8 ± 0.8 ; n-butylisobutylamine (liq.), -51.6 ± 1.2 ; pyrazole (cryst.), $+28.3 \pm 1.1$; and imidazole (cryst.), $+14.6 \pm 0.8$ kcal./mole. The derived bond energies $E(\text{C-N}) = 74.7$ and $E(\text{C=N}) = 142.6$ kcal. are used to calculate the resonance energies of pyrazole and imidazole as 29.3 and 14.2 kcal./mole, respectively.

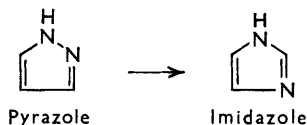
CALCULATION of the resonance energies, from bond energies, of unsaturated, heterocyclic compounds containing nitrogen have been hampered because of the lack of a reliable value for the bond energy $E(\text{C=N})$. In 1948, Coates and Sutton¹ reported the heat of

* Part V, *J.*, 1961, 3793.

¹ Coates and Sutton, *J.*, 1948, 1187.

combustion of *n*-butylisobutyraldimine, $\text{Bu}^n\text{N}=\text{CHPr}^i$, and from this calculated a value for $E(\text{C}=\text{N})$, which has been questioned by Cox, Challoner, and Meetham.² Calorimetric techniques, used in determining heats of combustion, have become more refined since these measurements were made. By taking advantage of these developments, it has been possible to obtain a more accurate heat of combustion of the imine and so establish a value for $E(\text{C}=\text{N})$. The heat of combustion of the hydrogenation product of *n*-butylisobutylamine, $\text{Bu}^n\text{Br}^i\text{NH}$, has also been measured, so as to obtain a value for the bond energy $E(\text{C}-\text{N})$.

Although the heats of combustion of a large number of substituted tetrazoles and some triazoles have been reported,³ there appear to be no data for the diazoles, pyrazole, and imidazole. The heats of combustion of these compounds have been measured, and have been used to calculate the heat of isomerisation, ΔH_i , and also the resonance energies of the two isomers.



EXPERIMENTAL

Compounds.—*n*-Butylisobutyraldimine was prepared by adding *n*-butylamine (1 mol.) to isobutyraldehyde (1 mol.). The imine was distilled through a 6-in. Fenske column. It had b. p. $139.0^\circ/752$ mm. *n*-Butylisobutylamine was prepared from the aldimine by reduction with (a) hydrogen, in presence of palladium-charcoal, and (b) lithium aluminium hydride in dry ether. The amine was distilled through a 6-in. Fenske column. It had b. p. $148.0^\circ/753$ mm.

Pyrazole (L. Light and Co., Ltd.) and imidazole (Kodak Ltd.) were recrystallised from light petroleum. They had m. p. 70° and $89.0\text{--}89.5^\circ$, respectively. Heilbron and Bunbury⁴ give $69.5\text{--}70.0^\circ$ and $88.0\text{--}89.0^\circ$, respectively.

Vapour Pressures.—The vapour pressure of *n*-butylisobutylamine has been measured over the temperature range $40\text{--}150^\circ$. It is given by the equation $\log_{10} p$ (mm.) = $-A/T + B$, where $A = 2154$ and $B = 7.99$. The derived latent heat of vaporisation (liquid to vapour), given by $\Delta H_{\text{vap.}} = 4.57A \times 10^{-3}$ kcal./mole, is 9.8 ± 0.3 kcal./mole.

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.⁵ The liquid *n*-butylisobutylamine and four samples of *n*-butylisobutyraldimine were sealed in Melinex bags. Two samples of *n*-butylisobutyraldimine were sealed in glass ampoules. The solid pyrazole and imidazole were compressed into pellets. All combustions were initiated by a platinum wire and cotton-thread fuse. For the combustion of *n*-butylisobutyraldimine in glass ampoules there was an additional fuse of oil.

The bomb was charged with oxygen to an initial pressure of 30 atm., and with 1.0 ml. of water. Each sample was fired at 25° .

Analysis.—After each combustion the bomb gases were analysed for carbon dioxide, to an accuracy of $\pm 0.02\%$. The bomb-washings were titrated with 0.1*N*-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 energy equivalent of the calorimeter was determined by combustion of a sample of benzoic acid, having $-\Delta U_b = 6.3181 \pm 0.0007$ kcal./g. The heats evolved in the following processes were taken to have the values given: (a) the formation of 0.1*N*-nitric acid from nitrogen, oxygen, and water, 13.81 kcal./mole;⁶ (b) the combustion of cotton fuse, 3.88 kcal./g.;⁷ (c) the combustion of Melinex, 1052.9 kcal./mole, *i.e.*,

² Cox, Challoner, and Meetham, *J.*, 1954, 265.

³ Williams, McEwan, and Henry, *J. Phys. Chem.*, 1957, **61**, 261.

⁴ Heilbron and Bunbury, "Dictionary of Organic Compounds," Eyre and Spottiswoode, London, 1953.

⁵ Fletcher, Mortimer, and Springall, *J.*, 1959, 580.

⁶ Prosen, "Experimental Thermochemistry," Interscience Publ. Inc., New York, 1956, Chap. 6.

⁷ Coops, Jessup, and van Nes, *ref. 6*, Chap. 3.

(C₁₀H₄O₄)_n/n;⁸ (d) the combustion of oil of empirical formula CH_{1.891}, 10·9838 kcal./g. (this sample was supplied by Dr. J. P. McCullough, United States Department of the Interior, Bureau of Mines, Bartlesville, Oklahoma, and was designated U.S.B.M.-P3a).

Results.—The results of the combustions are given in Table 1—4, in which the symbols have the same meanings as in Part II of this series.⁹ In addition, the following terms are used

TABLE 1.
n-Butylisobutyraldimine; *M*, 127·224.

Expt.	1	2	3	4	5	6
Wt.* of sample (g.)	0·683674	0·537662	0·804328	0·567704	0·786031	0·940774
Δ <i>R</i> _c (ohm)	0·18773	0·14474	0·21205	0·15340	0·20834	0·24873
CO ₂ obs. : calc. (%)	99·76	99·90	99·80	99·83	99·76	99·77
<i>q</i> _f (cal.)	5·74	4·85	5·35	6·19	7·88	5·21
<i>q</i> _m (cal.)	—	320·37	—	367·69	350·92	400·10
<i>q</i> _o (cal.)	563·29	—	315·45	—	—	—
<i>q</i> _n (cal.)	6·29	5·63	7·12	5·40	7·58	5·47
<i>q</i> _w (cal.)	1·46	1·01	1·61	1·09	1·60	1·89
<i>E</i> _c (cal./ohm)	11·44	9·97	13·46	10·40	13·10	16·01
−Δ <i>U</i> _c ^o (kcal./mole)	1299·92	1299·31	1298·67	1298·68	1298·98	1298·36

Mean −Δ*U*_c^o = 1299·11 kcal./mole (standard deviation of mean ± 0·24 kcal./mole).

* All weights *in vacuo*. *E*_s = 40154·0 cal./ohm; $\bar{s}E = \pm 0\cdot025\%$; $\bar{s}\Delta U_c^o = \pm 0\cdot019\%$; $\bar{s} = \pm 0\cdot031\%$; Δ*nRT* = −2·24 kcal./mole; −Δ*H*_c^o = 1301·35 ± 0·81 kcal./mole.

TABLE 2.
n-Butylisobutylamine; *M*, 129·240.

Expt.	1	2	3	4	5	6	7
Wt. of sample (g.) ...	0·427426	0·763539	0·720085	0·662350	0·693553	0·826095	0·653159
Δ <i>R</i> _c (ohm)	0·11922	0·20867	0·19667	0·18318	0·19136	0·22404	0·18073
CO ₂ obs. : calc. (%) ...	99·99	99·80	99·95	99·99	99·81	99·62	99·99
<i>q</i> _f (cal.)	4·89	7·80	7·02	15·02	13·05	12·91	10·96
<i>q</i> _m (cal.)	324·73	432·23	375·02	425·87	434·16	397·39	431·90
<i>q</i> _n (cal.)	4·43	5·81	5·01	10·96	11·54	13·54	10·16
<i>q</i> _w (cal.)	0·61	1·21	1·03	1·01	1·18	1·97	1·00
<i>E</i> _c (cal./ohm)	0·93	2·94	2·58	2·23	2·43	3·37	2·17
−Δ <i>U</i> _c ^o (kcal./mole)	1346·70	1345·91	1348·84	1347·42	1349·16	1346·56	1346·65

Mean −Δ*U*_c^o = 1347·31 kcal./mole (standard deviation of mean ± 0·52 kcal./mole).

*E*_s = 40154·0 cal./ohm; $\bar{s}E = \pm 0\cdot025\%$; $\bar{s}\Delta U_c^o = \pm 0\cdot038\%$; $\bar{s} = \pm 0\cdot046\%$; Δ*nRT* = −2·53 kcal./mole; −Δ*H*_c^o = 1349·84 ± 1·24 kcal./mole.

TABLE 3.
Pyrazole; *M*, 68·081.

Expt.	1	2	3	4	5
Wt. of sample (g.) ...	0·576164	0·548748	0·667691	0·489391	0·557868
Δ <i>R</i> _c (ohm)	0·09166	0·08861	0·10753	0·07853	0·09003
CO ₂ obs. : calc. (%) ...	98·52	99·72	100·00	99·13	99·97
<i>q</i> _f (cal.)	5·36	5·34	4·90	5·78	5·62
<i>q</i> _n (cal.)	9·72	9·87	15·74	11·35	14·12
<i>q</i> _w (cal.)	1·99	2·00	2·11	1·59	1·82
<i>E</i> _c (cal./ohm)	0·45	0·41	0·61	0·33	0·43
−Δ <i>U</i> _c ^o (kcal./mole) ...	446·64	447·80	445·16	447·15	445·93

Mean −Δ*U*_c^o = 446·54 kcal./mole (standard deviation of mean ± 0·46 kcal./mole).

*E*_s = 40809·1 cal./ohm; $\bar{s}E = \pm 0\cdot070\%$; $\bar{s}\Delta U_c^o = \pm 0\cdot103\%$; $\bar{s} = \pm 0\cdot124\%$; Δ*nRT* = −0·59 kcal./mole; −Δ*H*_c^o = 447·13 ± 1·11 kcal./mole.

here: *q*_m = heat of combustion of Melinex fuse; CO₂ obs. : calc. = the ratio of carbon dioxide recovered to that calculated for complete combustion of the sample and fuses. The mass of the sample burnt in each experiment was calculated from the mass of carbon dioxide formed, it being assumed that the fuses had burnt completely.

⁸ Evans and Skinner, *Trans. Faraday Soc.*, 1959, **55**, 256.

⁹ Bedford and Mortimer, *J.*, 1960, 1622.

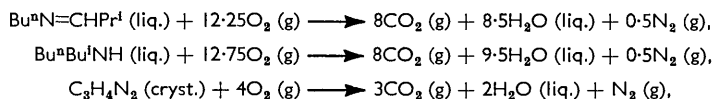
TABLE 4.
 Imidazole; *M*, 68-081.

Expt.	1	2	3	4	5
Wt. of sample (g.) ...	0.638603	0.579720	0.627143	0.638823	0.614802
ΔR_c (ohm)	0.09983	0.09095	0.09795	0.09989	0.09633
CO ₂ obs. : calc. (%) ...	99.93	99.94	99.91	99.74	99.93
q_l (cal.)	5.24	5.90	5.86	5.87	6.21
q_n (cal.)	15.05	15.82	12.51	17.47	14.00
q_w (cal.)	2.06	1.87	2.03	2.06	2.00
E_c (cal./ohm)	0.54	0.45	0.52	0.54	0.50
$-\Delta U_c^0$ (kcal./mole) ...	432.30	433.16	432.16	432.91	433.21

Mean $-\Delta U_c^0 = 432.75$ kcal./mole (standard deviation of mean ± 0.24 kcal./mole).
 $E_s = 40809.1$ cal./ohm; $\bar{s}E = \pm 0.070\%$; $\bar{s}\Delta U_c^0 = \pm 0.056\%$; $\bar{s} = \pm 0.090\%$; $\Delta nRT = -0.59$ kcal./mole; $-\Delta H_c^0 = 433.34 \pm 0.78$ kcal./mole.

Values of CO₂ obs. : calc. which were less than 100% may be due to (i) the presence of some organic impurity having a carbon content which is less, per gram, than that of the compound under investigation; (ii) the presence of some non-combustible impurity, probably water; or (iii) incomplete combustion of the sample. Since some combustions for each of the compounds gave values of CO₂ obs. : calc. of 99.90%, or greater, it seems more probable that the lower values of CO₂ obs. : calc. were due to either of causes (ii) and (iii). In each case the uncertainty associated with the ΔH_c^0 value is twice the standard deviation of the mean.

The combustions refer to the reactions:



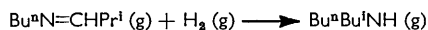
where C₃H₄N₂ refers to either pyrazole or imidazole.

Using the ΔH_f^0 values at 25°: H₂O (liq.), -68.3174 ; and CO₂ (g), -94.0518 kcal./mole,¹⁰ we calculate the following ΔH_f^0 values at 25°: n-butylisobutyraldimine (liq.), -31.8 ± 0.8 ; n-butylisobutylamine (liq.), -51.6 ± 1.2 ; pyrazole (cryst.), $+28.3 \pm 1.1$; and imidazole (cryst.) $+14.6 \pm 0.8$ kcal./mole.

DISCUSSION

The heat of combustion of n-butylisobutyraldimine reported here, $-\Delta H_c^0 = 1301.35 \pm 0.81$ kcal./mole, is about 0.5% higher than the value 1295 ± 2.4 kcal./mole measured by Coates and Sutton.¹ These workers made no quantitative analysis of the carbon dioxide produced on combustion. In the combustions reported here, the amount of carbon dioxide which was formed varied from 99.76 to 99.90% of the calculated quantity.

By incorporating an estimated¹ latent heat of vaporisation of 10.0 ± 0.5 kcal./mole for n-butylisobutyraldimine and our measured value of 9.8 ± 0.3 kcal./mole for n-butylisobutylamine, the heats of formation of the gaseous compounds are calculated as -21.8 ± 1.3 , and -41.8 ± 1.5 kcal./mole, respectively. From these data we obtain a heat of hydrogenation, ΔH_2 , of -20.0 ± 2.8 kcal./mole for the process



Jackman and Packham¹¹ have measured the heats of hydrogenation, in the liquid phase, of a number of imines R'N=CHR, where R' = Me, Et, or Prⁱ and R = Et, Prⁿ, or Prⁱ. The values fall within the range -21.0 ± 0.7 kcal./mole. Unfortunately, the latent heats of vaporisation which are necessary to refer to the gaseous state have not yet been determined. However, it seems unlikely that the heats of hydrogenation in the gaseous

¹⁰ National Bureau of Standards, Circular 500, Washington, 1952.

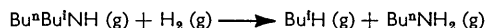
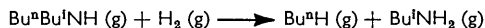
¹¹ Jackman and Packham, *Proc. Chem. Soc.*, 1957, 349.

state will differ from those in the liquid state by more than ± 0.5 kcal./mole, so that these values would be in close agreement with our value for the compound in which $R' = \text{Bu}^n$ and $R = \text{Pr}^i$.

If it is assumed that this heat of hydrogenation depends only on changes in bond energies, corresponding to bonds being broken or formed, then we may write

$$\Delta H_2 = E(\text{H-H}) + E(\text{C=N}) - E(\text{C-N}) - E(\text{N-H}) - E(\text{C-H})$$

Incorporating the values $E(\text{H-H})$, 104.2; $E(\text{N-H})$, 93.4; and $E(\text{C-H})$, 98.7 kcal./mole,¹² the difference $[E(\text{C=N}) - E(\text{C-N})] = 67.9$ kcal./mole is obtained. A value for $E(\text{C-N})$ may be calculated in terms of the heats, ΔH_3 and ΔH_4 , of the reactions



Using the relations

$$\Delta H_3 \text{ or } \Delta H_4 = E(\text{H-H}) + E(\text{C-N}) - E(\text{C-H}) - E(\text{N-H}),$$

and the $\Delta H_f^0(\text{g})$ values: $\text{Bu}^n\text{Bu}^i\text{NH}$, -41.8 ± 0.8 ; Bu^nNH_2 , -22.5 ± 0.27 , Bu^iNH_2 , -25.2 ± 0.22 ;¹³ Bu^nH , -30.15 ; and Bu^iH , -32.15 kcal./mole,¹⁴ we derive the values $E(\text{C-N}) = 74.3$ or 75.0 kcal./mole. Taking the mean value $E(\text{C-N}) = 74.7$ kcal./mole, we obtain $E(\text{C=N}) = 142.6$ kcal./mole.

The resonance energies, E_R , of pyrazole and imidazole may be calculated from the relation

$$E_R = -\Delta H_f^a(\text{g}) - E(\text{b}),$$

where $\Delta H_f^a(\text{g})$ is the heat of formation of the gaseous compound from the atoms, and $E(\text{b})$ is the sum of the bond energies for the bonds in the molecule. The latent heats of sublimation of pyrazole and imidazole have not been measured, but from boiling and melting points values are estimated as 15.0 ± 1.0 and 16.0 ± 1.0 kcal./mole, respectively. The heats of formation of gaseous pyrazole and imidazole are calculated as $+43.3 \pm 2.1$ and $+30.6 \pm 1.8$ kcal./mole, respectively. These values lead to a heat of gas-phase isomerisation, ΔH_i , of -12.7 ± 3.9 kcal./mole. Taking the following heats of formation of the atoms: C, 170.89; H, 52.09; and N, 112.9 kcal./g.-atom,¹² together with the additional bond energy values;¹² $E(\text{N-N})$, 39.0; $E(\text{C-C})$, 82.6; and $E(\text{C=C})$, 145.8 kcal., we calculate E_R values of 29.3 and 14.2 kcal./mole, for pyrazole and imidazole, respectively.

We thank Dr. H. A. Skinner for pointing out the need to determine the heat of combustion of *n*-butylisobutyraldimine and for suggesting that a value for the heat of hydrogenation to the corresponding amine would provide a useful check on the reliability of the results. One of us (P. B. E.) thanks the Institute of Petroleum for a Research Studentship, and another (A. F. B.) thanks the Department of Scientific and Industrial Research for a grant.

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¹² Cottrell, "The Strengths of Chemical Bonds," Butterworths Scientific Publns., 2nd edn., London, 1958.

¹³ Evans, Fairbrother, and Skinner, *Trans. Faraday Soc.*, 1959, **55**, 399.

¹⁴ American Petroleum Institute Research Project 44, Carnegie Press, Pittsburg, Pa., 1953.