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The enthalpy of formation of 4-nitrophenyl azide

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Abstract

The enthalpy of combustion of crystalline 4-nitrophenyl azide has been determined by static oxygen bomb calorimetry at 298.15 K as $-(3241.4 \pm 4.2)$ kJ mol^{-1}. The corresponding enthalpies of formation using an estimated enthalpy of sublimation are $\Delta_f H^0_m = (308.7 \pm 4.3)(c)$ and $(389.7 \pm 5.2)(g)$ kJ mol^{-1}. The predictive capacity of the Laidler and Pedley bond energy schemes as applied to organic azides is explored. © 1997 Elsevier Science B.V.

Keywords: Bond energy schemes; Heat of formation; Organic azides

Published thermochemical data on organic azides in modern compilations are confined to values for the enthalpies of formation of two alicyclic compounds, cyclopentyl azide and cyclohexyl azide [1] and the aliphatic 2-azidoethanol [2]. In order to compare the ($C–N_3$) bond enthalpy terms in aliphatic and benzenoid compounds, the enthalpy of formation of 4-nitrophenyl azide has been determined by oxygen combustion calorimetry.

4-Nitrophenyl azide was prepared by the addition of an aqueous solution of sodium azide to a solution of 4-nitrophenyldiazonium sulphate (obtained by diazotization [3] of 4-nitroaniline in sulphuric acid) [4]. The precipitated solid was separated by filtration, purified by four crystallizations from ethanol (melting temperature 72°C; literature 72.0 to 72.5°C [4], 74°C [5]), and stored in the dark to avoid photodecomposition [4]. The mole fraction purity was assessed as 0.9994 by differential scanning calorimetry (DSC). Two estimates of the enthalpy of fusion were obtained during this procedure, 17.0 and 17.2 kJ mol^{-1}; we adopt (17.1 ± 0.2) kJ mol^{-1} for this quantity.

The energy of combustion was determined using a static-bomb combustion calorimeter in the isoperibol mode [6,7]. Combustion proceeded violently under normal conditions, even when the oxygen pressure was reduced from 3 to 2 MPa, but clean combustions were obtained when 4-nitrophenyl azide was mixed with an equal or greater mass of benzoic acid. About 0.4 g of the azide and 0.6 g of thermochemical standard benzoic acid were accurately weighed into a tablet press and the mixture stirred thoroughly with a steel needle. After the tablet had been pressed it was weighed and stored in a desiccator. To determine the masses of azide and of benzoic acid not included in the tablet, the press and the needle were washed with ethanol to dissolve the remaining traces of the two compounds, and the washings analysed for 4-nitrophenyl azide by UV-spectrophotometry

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($\lambda_{max} = 310\,\mathrm{nm}$, where benzoic acid has negligible absorption).

The procedure for a determination was in all respects as described in Ref. [7]: completeness of combustion in the bomb (volume 0.346 dm^3) containing 10 cm^3 of water and an oxygen pressure of 3 MPa was demonstrated by the absence of soot in the products. The energy equivalent of the calorimeter was determined by the combustion of thermochemical standard benzoic acid (Bureau of Analysed Samples Ltd, Batch 190k) as $(9.3741 \pm 0.0014)\,\mathrm{kJ\,K^{-1}}$.

The specific heat capacity of 4-nitrophenyl azide was determined over the temperature range 310 to 330 K by DSC. The results are represented by the relation

$$c_p/\mathrm{J\,g^{-1}\,K^{-1}} = 0.343 + 0.0022\,T/\mathrm{K}$$

from which the value at 298.15 K ($1.00\,\mathrm{J\,g^{-1}\,K^{-1}}$) was obtained by extrapolation. The value $\rho/\mathrm{g\,cm^{-3}} = 1.30$ at 298.15 K was calculated from the dimensions of weighed cylindrical tablets.

Energy corrections for the combustion of benzoic acid were based on the value $\Delta_c u^0 = -(26.4128 \pm 0.0025)\,\mathrm{kJ\,g^{-1}}$ (obtained by correction of the certified value under standard bomb conditions to standard state conditions) and amounted to approximately 63% of the total measured energy change.

From seven determinations the mean value $\Delta_c u^0 = -(19.780 \pm 0.025)\,\mathrm{kJ\,g^{-1}}$ was obtained[2] for the reaction

$$\begin{aligned} &C_6H_4N_4O_2(c) + 6O_2(g) \\ &\quad = 6CO_2g + 2H_2O(l) + 2N_2(g) \end{aligned}$$

The following molar (molar mass $=164.124\,\mathrm{g\,mol^{-1}}$) quantities were derived:

$$\Delta_c U^0_m = -(3246.4 \pm 4.2)\,\mathrm{kJ\,mol^{-1}}$$

$$\Delta_c H^0_m = -(3241.4 \pm 4.2)\,\mathrm{kJ\,mol^{-1}}$$

$$\Delta_f H^0_m(c) = -(308.7 \pm 4.3)\,\mathrm{kJ\,mol^{-1}}$$

Standard enthalpies of formation of $CO_2(g)$ and $H_2O(l)$ were taken from the *CODATA* compilation [8].

The bond enthalpy for the C–N_3 bond in 4-nitrophenyl azide has been compared with the corresponding bond enthalpies in aliphatic and alicyclic compounds using (i) the well-established Laidler bond energy scheme [9] and (ii) the recently developed Pedley scheme [10]. Both of these procedures enable a composite bond enthalpy term, E(C–N_3), which is the sum of the bond enthalpies of the C–N and the two N–N bonds, to be evaluated. For these calculations we have assumed a value for the enthalpy of sublimation of 4-nitrophenyl azide of $(81 \pm 3)\,\mathrm{kJ\,mol^{-1}}$ at 298.15 K, by analogy with the known value for 1,3-dinitrobenzene [11]. These authors [11] used an effusion manometric method in their study and reported a value of $(81.2 \pm 1.7)\,\mathrm{kJ\,mol^{-1}}$ at 323 K for the enthalpy of sublimation of 1,3-dinitrobenzene.

Laidler's scheme does not include a value for the aromatic carbon to NO_2 bond enthalpy (E(C_b–NO_2) in his notation) so this term was determined, using the known value of $\Delta_f H^0_m(C_6H_5NO_2, g)$, as 1188 $\mathrm{kJ\,mol^{-1}}$. This result was assumed to be transferable to the corresponding bond in 4-nitrophenyl azide. The justification for this assumption is that E(C–NO_2) shows little dependence on the nature of the carbon atom, since the values of E(C–NO_2)/$\mathrm{kJ\,mol^{-1}}$ (Laidler) in CH_3NO_2, $C_2H_5NO_2$ and $C_3H_7NO_2$ are 1182, 1189 and 1192, respectively, values that are close in magnitude to E(C_b–NO_2)/$\mathrm{kJ\,mol^{-1}}$.

Table 1 lists values for E(C–N_3) obtained using both Laidler's and Pedley's schemes. The agreement between the Laidler and Pedley schemes is satisfactory, except for 4-nitrophenyl azide, the only benzenoid compound. This suggests that, for disubstituted benzenes at least, the Pedley and Laidler schemes will

Table 1
Bond enthalpy terms in organic azides at 298.15 K

Compound	E(C–N_3)[a]/kJ $\mathrm{mol^{-1}}$	
	Laidler	Pedley [b]
2-azidoethanol [c]	1246	1244
4-nitrophenyl azide	1300	1283
Cyclopentyl azide [c]	1310	1312
Cyclohexyl azide [c]	1329	1332

[a] Estimated uncertainty intervals in these values is ±5 $\mathrm{kJ\,mol^{-1}}$.
[b] Pedley's notation for these values is $[F(N_3) + B(C - N_3)]$ – see appendix.
[c] The enthalpies of formation for these species were taken from [9] with an estimated enthalpy of vaporization for 2-azidoethanol (45 $\mathrm{kJ\,mol^{-1}}$ as in 2-chloroethanol).

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[2] Throughout this paper uncertainty intervals of reported experimental results denote 95% confidence limits, calculated using student's t at the appropriate number of degrees of freedom.

yield different estimates for standard enthalpies of formation. Pedley [10] has stated that his scheme may not apply to polyfunctional benzenoid compounds, particularly those with nitrogen-containing substituents. Given the uncertainties in these bond enthalpy terms, there is clearly no significant difference in the values of $E(C\text{–}N_3)$ in the final three compounds in the table, which include both benzenoid and aliphatic species. It is apparent, however, that $E(C\text{–}N_3)$ in 2-azidoethanol differs significantly from the values in the other compounds considered. Details of the calculation for 4-nitrophenyl azide are given in an Appendix A.

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Appendix A

Application of the Laidler [9] and Pedley [10] bond energy schemes to 4-nitrophenyl azide.

Laidler distinguishes between bond energy terms where H is bonded to primary, secondary, tertiary, and benzenoid carbon atoms (see Table 50 in Ref. [9] for a list of parameters). Also included are composite terms where C is bonded to a functional group, e.g. $C\text{–}NO_2$, $C\text{–}SO_2$. Laidler did not include a term for NO_2 bonded to benzenoid C, $E(C_b\text{–}NO_2)$ in his notation and this term is estimated from the known value of the enthalpy of formation of nitrobenzene [10] in the following general equation,

$$\Delta H_f^0[\text{compound, g}] = \Sigma\Delta H_f^0[\text{elements, g}] - \Sigma E_i$$

where E_i are individual bond energy terms. Using the abbreviation, $\Delta H_f[X, g] = [X]$,

$$\begin{aligned}[C_6H_5NO_2] &= 6[C] + 5[H] + [N] + 2[O] \\ &\quad - E(C_b - NO_2) - 5E(C_b - H) \\ &\quad - 6E(C_b - C_b).\end{aligned}$$

Using enthalpies of formation of the gaseous elements from Table 24 in Ref. [9], $E(C_b - NO_2) = 1188.5\,\text{kJ mol}^{-1}$. Substituting this value in the general expression written for 4-nitrophenyl azide, we have

$$\begin{aligned}[N_3C_6H_4NO_2] &= 6[C] + 4[H] + 4[N] + 2[O] \\ &\quad - E(C_b - NO_2) - 4E(C_b - H) \\ &\quad - 6E(C_b - C_b) - E(C_b - N_3)\end{aligned}$$

from which $E(C_b - N_3) = 1300\,\text{kJ mol}^{-1}$.

In contrast to Laidler, Pedley uses fixed values for all bond energy terms ($B(i, j)$ where i and j are the bonded atoms) irrespective of their environment. He defines fragment energies [$F(i)$] which are composite terms including bonds in different environments, e.g. $F(\text{–}CH_3)$, $F(>CH_2)$, $F(\text{–}OH)$, $F(>C=O)$ etc. In addition 3-component interactions [$C(ijk)$] are defined and are called bond interactions. This scheme has a formal similarity with that of Allen [9] but through the optimization of a large body of experimental data the number of $C(ijk)$ terms required is minimised with many defined as zero. Applying the general equation to 4-nitrophenyl azide:

$$\begin{aligned}[N_3C_6H_4NO_2] &= 6[C] + 4[H] + 4[N] + 2[O] \\ &\quad - E(C_b - NO_2) - 4F(-CH=) \\ &\quad - 2F(>C=) - F(NO_2) - F(N_3) \\ &\quad - 3B(-C=C-) - 3B(=C-C=) \\ &\quad - B(C_{ar} - NO_2) - B(C_{ar} - N_3) + R(C_6H_6),\end{aligned}$$

from which $[F(N_3) + B(C_{ar} - N_3)] = 1283\,\text{kJ mol}^{-1}$. All numerical input for this calculation are given in Tables 2.1 through 2.4 in Ref. [10]. The subscript ar (not used by Pedley) indicates an aromatic atom. $R(C_6H_6)$ is the resonance correction for the aromatic ring (Table 2.8 of Ref. [10]). Pedley uses the notation $A(C_6H_4N_4O_2)$ for $6[C] + 4[H] + 4[N] + 2[O]$.

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