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# Enthalpies of Combustion of Organic Compounds. III.* D-, L- and DL-Alanines

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**Synopsis.** Enthalpies of combustion of D-, L- and DL-alanines were measured by oxygen static bomb calorimetry. Derived thermodynamic quantities at 298.15 K for D-, L- and DL-isomers are as follows: $\Delta E_c^\circ = -1619.24 \pm 0.58$, $-1620.26 \pm 0.63$ and $-1617.97 \pm 0.50$ kJ mol$^{-1}$; $\Delta H_c^\circ = -1619.86 \pm 0.58$, $-1620.88 \pm 0.63$ and $-1618.59 \pm 0.50$ kJ·mol$^{-1}$; $\Delta H_f^\circ(c) = -561.08 \pm 0.71$, $-560.06 \pm 0.76$ and $-562.35 \pm 0.65$ kJ mol$^{-1}$, respectively.

Measurements of heats of combustion of alanine, one of the fundamental amino acids, have been made on L-isomer by Tsuzuki *et al.*[1] and on L- and DL-isomers by Huffman *et al.*[2,3] On L-isomer, the value of $\Delta H_c^\circ$ by Tsuzuki *et al.*[1] differs significantly from that by Huffman *et al.*[2] up to about 3%. On D-isomer there appeared no report hitherto. In this paper the enthalpies of combustion of D-, L- and DL-alanines in their crystalline states are reported. The idealized combustion reaction to which the energies and enthalpies of combustion given in this paper refer is the following one at 25 °C:

$$C_3H_7O_2N(c) + (3.75)O_2(g) = 3CO_2(g) + (3.5)H_2O(l) + (0.5)N_2(g).$$

## Experimental

*Materials.* L-Alanine (Takara Kôsan Co., Ltd.), D-alanine (Ajinomoto Co., Ltd.) and DL-alanine (Nakarai Chemicals, Ltd.) were purified by recrystallization from aqueous solutions, twice, twice and four times, respectively. After the samples were first dried under vacuum (~0.1 kPa), they were pelletted and then stored for 6 months in a desiccator over anhydrous magnesium perchlorate. Specific rotatory power of the solutions ($c = 0.022$ mol dm$^{-3}$ in 2.0 M HCl) was as follows: $[\alpha]_D^{20} = +14.3°$ (L-isomer), $-14.4°$ (D-isomer) and $-0.2°$ (DL-isomer), respectively. Each peak in the X-ray diffraction patterns obtained by using Cu-K$\alpha$ radiation coincided with that calculated from the crystallographic data.[4,5]

*Apparatus, Procedures and Calculation.* An isoperibol rotating precision bomb-calorimeter reported previously[6] was used without rotation. It was pointed out, however, by Huffman *et al.*[2,3] that alanine was very troublesome to burn as it had a decided tendency to jump out of the crucible when burned partially. So, we designed a special deep crucible with a baffle (Pt-10% Rh), having the density and the specific heat capacity of 20.50 g cm$^{-3}$ and 0.1464 J K$^{-1}$ g$^{-1}$ at 25 °C, respectively, (Fig. 1) and used it to facilitate complete combustion by keeping off such a jumping-out as described above. The energy equivalent was defined for the system made up of an empty bomb and a gimbal as before and was found from 13 calibration-experiments with benzoic acid (Standard Reference Material 39i, National Bureau of Standards, U.S.A.) to be 15159.78±0.57 J K$^{-1}$, where uncertainty is the standard deviation of the mean. To make the combustion of the alanine sample more perfect, *ca.* 0.15 g of liquid paraffin (Wakô Pure Chemical Co., Ltd.) was used as promotor in each experiment. In this way we succeeded in performing perfect combustion. In order to make the ignition procedure reproducible in every run, we used two electrical timers: one for timing the begining and the other for timing the ending of ignition, respectively. Calculation was carried out as before. NEAC 2200 electronic computor of Osaka University was used to calculate Washburn corrections and to obtain the final data of energy of combustion.

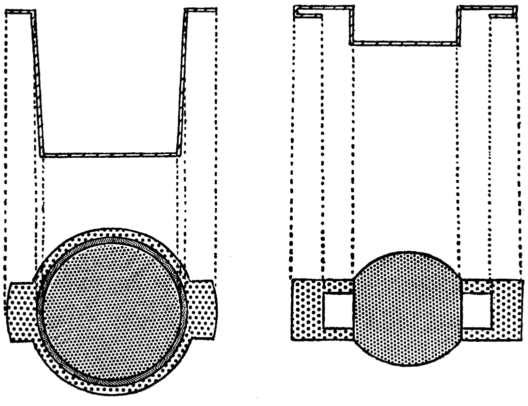
(a) (b)

Fig. 1. (a) Crucible, (b) Baffle. (Scale, 14/17)

TABLE 1. AUXILIARY DATA FOR THE CALCULATION OF ENERGY OF COMBUSTION

| | | $\rho$/g cm$^{-3}$ | $c_p$/J K$^{-1}$ g$^{-1}$ | $(\partial E/\partial P)_T$/ J kPa$^{-1}$ g$^{-1}$ |
|---|---|---|---|---|
| Alanine | $C_3H_7O_2N$ | 1.37 | 1.372 | (−0.957)[a] |
| Fuse | $CH_{1.860}O_{0.930}$ | 1.5 | 1.70 | −2.94 |
| Auxiliary oil | $CH_{1.885}$ | 0.8824 | 2.22 | −2.60 |
| Pt-10% Rh | —— | 20.50 | 0.1464 | —— |

a) The value in bracket is estimated one.

*Auxiliary Quantities.* Auxiliary data adopted in the calculation of $\Delta E_c^\circ$, *i.e.* the composition formula and the values (for 25 °C) of density, $\rho$, of specific heat capacity, $c_p$, and of $(\partial E/\partial P)_T$ for the combustible substances, are given in Table 1. Other auxiliary data used are as follows: $M$(compd.) = 89.0947 g mol$^{-1}$, $m$(Pt) = 29.511 g, $V$(bomb) = 0.3458 dm$^3$, $\Delta E_c^\circ/M$(fuse) = −16507 J g$^{-1}$, $\Delta E_c^\circ/M$(oil) = 45909.3±4.1 J g$^{-1}$, where uncertainty is standard deviation of the mean. Six combustion experiments were carried out for D-, L- and DL-alanines, respectively. Data from combustions selected as typical are given in Table 2. Notations in Table 2 follow those by Hubbard *et al.*[7] except for the followings: $\Delta m$(H$_2$O cal.), excess water in the calorimeter can; $\Delta E$ (std. state), sum of items 81—85, 87—89, 93 and 94 in Ref. 7. The results of the individual combustion experiment in terms of $\Delta E_c^\circ$ at 298.15 K are summarized as follows: −1618.83, −1619.90, −1619.43, −1619.68, −1619.04, −1618.54, mean and standard deviation of the mean −1619.24±0.21 kJ mol$^{-1}$ for L-alanine; −1620.55,

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−1620.38, −1619.66, −1620.07, −1621.25, −1619.65, mean and standard deviation of the mean −1620.26± 0.25 kJ mol$^{-1}$ for D-alanine; −1617.55, −1617.88, −1618.09, −1618.46, −1618.27, −1617. 57, mean and standard deviation of the mean −1617.97±0.15 kJ mol$^{-1}$ for DL-alanine. Thermochemical quantities were calculated from those results and given in Table 3. In the calculation of the standard enthalpies of formation of the present samples, CODATA key values[8)] for the standard enthalpies of formation at 298.15 K of $H_2O(1)$ and $CO_2(g)$; $\Delta H_f°(H_2O, 1) = -285.30 \pm 0.042$ kJ mol$^{-1}$, $\Delta H_c°(CO_2, g) = -393.51 \pm 0.13$ kJ mol$^{-1}$ were employed, where uncertainties represent the Task Group's estimates of the overall uncertainties at a 95 per cent confidence level. The standard enthalpy ot formation of L-isomer in the gaseous state was calculated by using a enthalpy of vaporization reported by Svec *et al.*[9)] All the uncertainties in this paper are uncertainty interval. recommended by Rossini,[10)] *i.e.* twice the final overall standard deviation of the mean, unless specified.

## Discussion

In Table 4 our data are compared with those of Huffman *et al*[2),3)] and Tsuzuki *et al.*[1)] The difference between the $\Delta H_c°$ values of Huffman *et al.*[2)] and of the present work for L-alanine is well within the sum of each uncertainty interval. But these values are quite far from that of Tsuzuki *et al.*,[1)] the descrepancy being no less than 3%. The value of $\Delta H_c°$ of D-alanine observed in this work also coincides with those of L-alanine by Huffman *et al.*[2)] and by the author within the sum of each uncertainty interval. Thus, as in the case of glutamic acid, previously described by two of the authors,[11)] it is also concluded that the $\Delta H°$ values of different optical isomers of alanine coincide with each other. The $\Delta H_c°$ value of DL-alanine of this work is in good agreement with that of Huffman *et al.*[3)] within the uncertainty interval.

Table 2. Typical results in combustion experiments

| Compound<br>Exp. No. | L-Alanine<br>L-5 | D-Alanine<br>D-5 | DL-Alanine<br>DL-4 |
|---|---|---|---|
| $m^i$(compd.)/g | 1.19068 | 1.18150 | 1.17692 |
| $m^i$(fuse)/g | 0.00298 | 0.00320 | 0.00293 |
| $m^i$(oil)/g | 0.11281 | 0.15223 | 0.13143 |
| $m^i(H_2O$ tot.)/g | 1.226 | 1.204 | 1.191 |
| $\Delta m(H_2O$ cal.)/g | 0.027 | −0.014 | 0.032 |
| $p^i$(gas)/MPa | 3.047 | 3.040 | 3.045 |
| $T_i$/°C | 23.19657 | 23.13588 | 23.17551 |
| $T_f$/°C | 24.99832 | 25.04563 | 25.01457 |
| $\Delta T_{corr}$/°C | 0.02867 | 0.02630 | 0.02657 |
| $n^f(HNO_3)$/mol | 0.000595 | 0.000696 | 0.000634 |
| $\Delta E_{ign}$/J | 3.3 | 5.9 | 2.9 |
| $\Delta E$(std. state)†/J | 14.0 | 14.5 | 14.1 |
| $\Delta E_{diln}(HNO_3)$/J | −0.1 | −0.1 | −0.1 |
| $\Delta E_{decomp}(HNO_3)$/J | 35.0 | 41.0 | 37.3 |
| $\varepsilon^i$(cont.)/J K$^{-1}$ | 21.48 | 21.44 | 21.36 |
| $\varepsilon^f$(cont.)/J K$^{-1}$ | 23.95 | 24.00 | 23.84 |
| $\Delta E_c°$/kJ mol$^{-1}$ | −1619.04 | −1620.55 | −1618.46 |

† items 81-85, 87-89, 93, 94 in Ref. 7.

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Table 3. Results and derived quantities at 298.15 K

| | L-Alanine | D-Alanine | DL-Alanine |
|---|---|---|---|
| $\Delta E_c°$/kJ mol$^{-1}$ | −1619.24±0.58 | −1620.26±0.63 | −1617.97±0.50 |
| $\Delta H_c°$/kJ mol$^{-1}$ | −1619.86±0.58 | −1620.88±0.63 | −1618.59±0.50 |
| $\Delta H_f°$ (c)/kJ mol$^{-1}$ | − 561.08±0.71 | − 560.06±0.76 | − 562.35±0.65 |
| $\Delta H_f°$ (g)/kJ mol$^{-1}$ | − 433.0 ±1.8 | —— | —— |

Table 4. The comparison of $\Delta H_c°$ value obtained by different investigators

| | L-Alanine | D-Alanine | DL-Alanine |
|---|---|---|---|
| This work | −1619.86±0.58 | −1620.88±0.63 | −1618.59±0.50 |
| Huffman *et al.*[2),3)] | −1619.71±0.54 | —— | −1617.37±0.57 |
| Tsuzuki *et al.*[1)] | −1577.0 ±2.1 | —— | —— |

The values of Huffman *et al.*[2),3)] and of Tsuzuki *et al.*[1)] were taken from Ref. 12.