Combustion Calorimetric Studies on Urea-Carboxylic Acid Inclusion Complexes

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Inclusion complexes of urea with several long-chain fatty acids (containing 10 to 22 C atoms) were prepared and their heats of combustion were measured using an isoperibol bomb calorimeter. The internal energy of combustion increases approximately linearly with the number of C atoms in the fatty acid used to make the complex.

Key Words: Combustion calorimetric studies, Urea-carboxylic acid, Complexes.

INTRODUCTION

Several studies have been reported on thermal properties of inclusion complexes of urea with long-chain compounds[1–9]. Differential scanning calorimetry, differential thermal analysis and thermogravimetric analysis have been carried out on these compounds. The studies have focussed on the decomposition behaviour of the complexes. Thus it was concluded that most of the compounds decompose either below the melting point of urea (132.7°C) or at this temperature, when the urea melts, releasing the guest molecule. However, the inclusion complexes formed with saturated fatty acids containing 20 carbon atoms or more are stable well above the melting point of urea. The present study deals with the enthalpy and internal change of combustion of these compounds measured in a bomb calorimeter.

EXPERIMENTAL

The procedures described in the literature[10–15] were used to prepare the inclusion compounds. A suitable mass of the carboxylic acid was added to a solution of excess urea in methanol with constant stirring and heating to obtain a clear solution. On cooling to room temperature (or at 0°C, if necessary), the solid complex separated out. Table-1 lists specific literature references to the method of preparation of all the complexes used in this study. The ratio acid : urea previously reported in the literature is included along with the reference.

TABLE-1
SUMMARY OF RESULTS
(Literature references are for the method of preparation and the host-guest ratios)

Acid	H, G in complex	MM complex	$-\Delta U$ (kJ/mol)	Reference
Decanoic acid	8.18	758	12.5	10
Dodecanoic acid	9.76	787	13.6	10
Tetradecanoic acid	11.0	815	14.3	10
Hexadecanoic acid	12.2	843	15.4	10
Octadecanoic acid	14.2	871	18.2	10
Eicosanoic acid	14.4	899	18.7	12
Docosanoic acid	15.6	927	19.5	15

The heat of combustion was measured on a Parr isoperibol bomb calorimeter[16] model 1266 with the Parr 1563 water handling system. The calorimeter consists of a steel combustion bomb, which can be immersed in water contained in a bucket. An air gap surrounds the bucket and around that gap is a jacket through which water at a fixed temperature is circulating continuously. The closed loop through which the water is circulating contains, besides the water jacket, the water handling system with a pump, a heater and a cooler. The system provides a uniform water supply circulating at constant temperature through the jacket.

In conventional adiabatic bomb calorimetery, the temperature in the jacket is continuously adjusted to match the temperature of the bucket before and after the combustion. In isoperibol bomb calorimetery, on the other hand, the calorimeter jacket is kept at a constant temperature (*ca.* 35°C) while heat from the combustion reaction increases the temperature of the water in the bucket. During the test the small amount of heat flowing between the bucket and its surroundings is monitored by a microprocessor in the calorimeter, which continuously applies corrections for the leak. The exact rise in temperature is then calculated after this correction is taken into account.

Procedure: The calorimeter is turned on and water allowed to pump into the jacket from the water handling system. The temperature of the water circulating in the jacket stabilizes at 35°C after about one hour. To standardize the calorimeter, around 1 g of pure benzoic acid is pressed into a pellet using a pellet press. The pellet is then weighed accurately on an analytical balance and placed in the crucible in the oxygen bomb. A length of 10 cm of fuse wire is connected between the terminals and allowed to touch the pellet. The bomb is sealed and filled with oxygen to 28 atm. pressure. The charged bomb is placed in 2000 ± 0.5 g of distilled water contained in a bucket and the ignition lead wires connected.

The sample is ignited and the temperature of the water in the bucket increases because of the released heat. The exact temperature increase (after the necessary corrections are applied by the microprocessor circuitry) is displayed at the end of the run. The heat capacity of the calorimeter was determined in a calibration run using analytical reagent grade benzoic acid. From the known amount of the energy of combustion of benzoic acid and the measured temperature rise, heat capacity of the calorimeter was calculated. The measurement was repeated using each of the fatty acid-urea complex samples. The energy of combustion was calculated per mole of the complex using the published values of the host-guest ratio (Table-1). The internal energy change on combustion was measured for each of the acids.

RESULTS AND DISCUSSION

A plot of ΔU for the combustion of the complex against the number of C atoms of the host carboxylic acid shows an approximate linear behaviour (Fig. 1). For comparison, handbook values of ΔU for the combustion of the pure carboxylic acids are plotted in the same figure. The pure fatty acids follow the linear behaviour more closely than the complexes. A possible explanation is that the values of host-guest ratios do not increase linearly with the number of C atoms. Fig. 2 shows a plot of the literature values of the ratio against the number of C atoms. A comparison of the two plots (Figs. 1 and 2) shows that the deviation from the linear behaviour in ΔU combustion mirrors the deviation for the host-guest ratio. The ratio is used to measure the molar mass of the complex needed to calculate the molar energy of combustion and any deviation in the linear behaviour in the host-guest ratio is reflected in ΔU of combustion per mole of the complex.
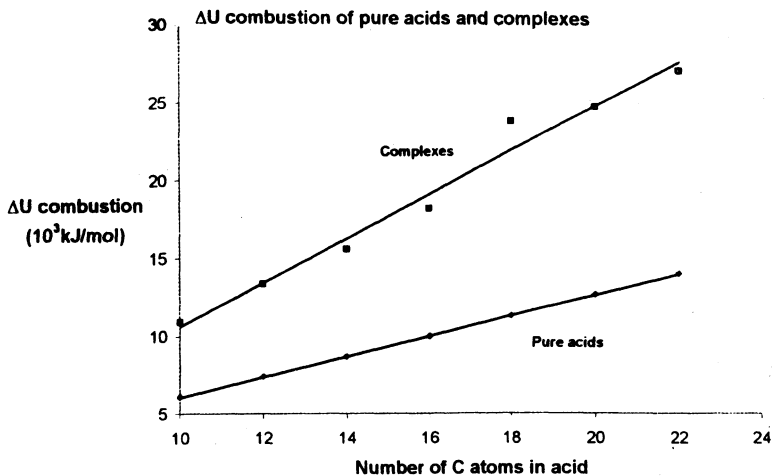

Fig. 1.   Internal energy of combustion for pure acids and complexes from C_{10} to C_{22}
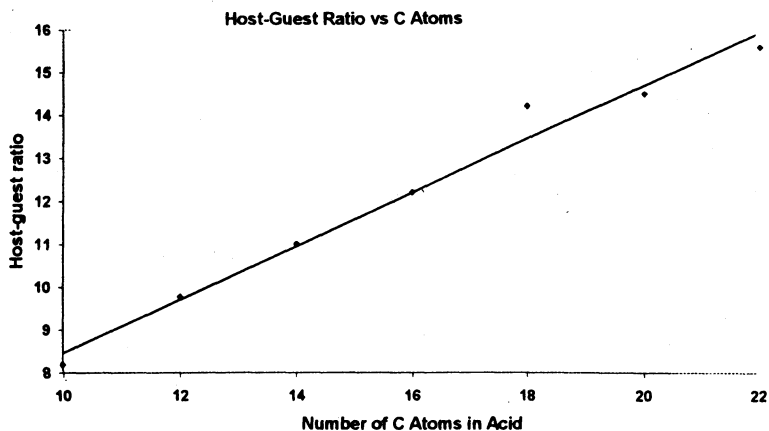

Fig. 2.   Plot of host-guest ratios against the number of C atoms in the acids

Repeated calorimetric measurements on benzoic acid gave values of the internal energy change on combustion reproducible to within 0.1 kJ/mol.   The limitation in precision comes from the larger uncertainty in the reported host-guest ratios (Table-1).

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REFERENCES

1.   O. Redlich, C.M. Gable, A.K. Dunlop and R.M. Miller, *J. Am. Chem. Soc.*, **72,** 4153 (1950).
2.   H.G. McAdie, *Can. J. Chem.*, **40,** 2195 (1962).
3.   ————, *Can. J. Chem.*, **41,** 2144 (1963).
4.   L.C. Fetterly, in: L. Mandelcorn (Ed.), Non-Stoichiometric Compounds, Academic Press, New York, p. 491 (1964).
5.   R.C. Pemberton and N.G. Parsonage, *Trans. Faraday Soc.*, **61,** 2112 (1965).
6.   Y. Chatani, H. Anraku and Y. Taki, *Mol. Cryst. Liq. Cryst.*, **48,** 219 (1978).
7.   K. Takemoto and N. Sonoda, in: J.L. Atwood, J.E.D. Davies and D.D. MacNicol (Eds.), Inclusion Compounds, Vol. 2, Academic Press, New York, p. 47 (1984).
8.   N.G. Parsonage and L.A.K. Staveley Sonoda, in: J.L. Atwood, J.E.D. Davies and D.D. MacNicol (Eds.) Inclusion Compounds, Vol. 3, Academic Press, New York, p. 1 (1984).
9.   R. Bishop and I.G. Dance, in: E. Weber (Ed.) Topics in Current Chemistry, Vol. 149, Springer-Verlag, Berlin, p. 137 (1988).
10.   W. Schlenk (Jr.) and J. Liebigs, *Ann. Chem.*, **565,** 204 (1949).
11.   H.U. Lenne, H.C. Mez and W. Schlenk (Jr.), *Chem. Ber.*, 101, 2453 (1968).
12.   H.L. Casal, *J. Phys. Chem.*, **89,** 4799 (1985).
13.   L.C. Fetterly, Ph.D. Dissertation, University of Washington, Seattle, (1950) presented at 26th Fall Meeting, Am. Oil Chemists' Soc., Cincinnati, Ohio (1952).
14.   M.F. Bengen, German Patent Appl. OZ 12438 (March 18, 1940); German Patent 869, 070 (1953). Tech Oil Mission Reel, **143,** 135 (1946).
15.   J. Ahmad, A.J. Freestone and A. Hussain, *J. Incl. Phenom. Mol. Recog. Chem.*, **18,** 115 (1994).
16.   Manufactured by Parr Instrument Co., Moline, Il, USA.