

HEATS OF COMBUSTION OF SOME SYMMETRICAL DIALKYL UREAS AND THEIR CORRESPONDING ALKYL CARBAMATES

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ABSTRACT

The standard heats of combustion of the disubstituted ureas, N, N'-diheptyl urea, N, N'-dioctyl urea and N, N'-didecyl urea and the carbamates, *n*-heptyl ammonium *n*-heptyl carbamate, *n*-octylammonium *n*-octyl carbamate and *n*-decyl ammonium *n*-decyl carbamate have been determined. The values found are 2353 ± 1.3 , 2658.4 ± 1.1 , 3268.5 ± 1.7 , 2349.8 ± 1.6 , 2654.4 ± 1.2 , 3264.6 ± 1.8 , K.cals. mole⁻¹ respectively. The heats of formation of these compounds have been calculated.

LACK of data on the heats of formation of symmetrical (N, N') dialkyl ureas and their respective alkyl ammonium alkyl carbamates has greatly hampered the calculation of the thermodynamic data of the reactions by which these compounds are produced. To evaluate the heats of formation of these compounds precise and accurate measurements of the heats of combustion are required. The present investigation reports experimental data on the heats of combustion of the ureas, N, N'-diheptyl urea, N, N'-dioctyl urea, N, N'-didecyl urea and the carbamates heptyl ammonium heptyl carbamate, octyl ammonium octyl carbamate and decyl ammonium decyl carbamate. The heats of formation of these compounds have also been calculated.

METHOD AND APPARATUS

The heats of combustion of the compounds were determined by the combustion of the solid ureas and the carbamates in the form of pellets in an oxygen bomb calorimeter.¹ The procedure followed is similar to that described in *A.S.T.M. Standards*² and by Dickinson.³ The sample was weighed in a nickel crucible and placed in the loop electrode. One millilitre of water was added to the bomb and the bomb was filled with oxygen to 25 atmospheric pressure at 25° C. The sample was ignited by means of a fuse wire coiled above the sample. The thermometers employed in the measurement of temperature were of the range 65-90° F. graduated in

units of 0.05°F . and provided with correction charts for scale correction. The temperature was read correct to 0.005°F . by suitable magnification. The corrections for thermal leakage, for the formation of nitric acid and the combustion of the fuse wire are applied by adopting the procedure given in the *Manual of the Parr Instrument Company*.¹ The energy equivalent of the calorimeter system was determined by employing benzoic acid as the standard substance. Five calorimetric experiments were made with each of the samples. The mean value and the average deviation from the mean are given in Table II. After the combustion there was no carbon left in the bomb indicating the completeness of the combustion.

MATERIALS

(a) *Substituted ureas*.—The substituted ureas are synthesised by the high pressure reaction of carbon dioxide with the corresponding primary amine.⁴ They were purified by recrystallisation from aqueous ethyl alcohol and dried over phosphorus pentoxide under reduced pressure.

(b) *Carbamates*.—The carbamates⁵ are obtained by passing dry carbon dioxide into an ethereal solution of the amine maintained at 0°C . The crystalline carbamate obtained was washed with fresh portions of dry ether to remove any unreacted amine and preserved in a desiccator over phosphorus pentoxide.

Amines.—The amines employed (*n*-heptyl, *n*-octyl and *n*-decyl amines) are prepared by the "Schmidt reaction"⁶ and purified by standard methods.

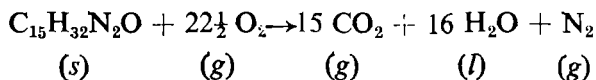
The results of the microcombustion analysis and the melting points of the ureas and carbamates are given in Table I which indicate that the samples are quite pure.

EXPERIMENTAL RESULTS

The results of the heats of combustion of the ureas and carbamates are listed in Table II. The values of the heats of combustion at constant volume, ΔE_c° in K.cals. mole⁻¹ at 25°C . are given in column 3 of Table II. These are converted to the corresponding values at constant pressure, ΔH_c° by employing the relation,

$$\Delta H_c^\circ = \Delta E_c^\circ + \Delta nRT$$
 where Δn is the increase in the number of moles of gas in the system. The last column contains values of the standard heats of formation from the elements, ΔH_f° , calculated from the heats of combustion, ΔH_c° , with the aid of the values of the heats of formation of carbon

dioxide and liquid water.¹⁰ The heat of combustion ΔE_c° , for instance in the oxidation of N, N'-diheptyl urea refer to the reaction,



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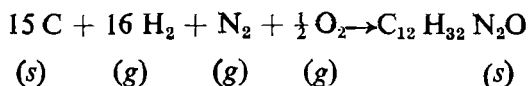


TABLE I

Melting points and microcombustion data

Compound	Melting point ° C.		Microcombustion analysis	
	Observed	Literature value	Found (%)	Theoretical (%)
N, N'-Diheptyl urea (C ₇ H ₁₅ NH) ₂ CO	91·0	91·0 ⁷	C = 69·72 H = 12·92 N = 11·0	C = 70·31 H = 12·51 N = 10·93
N, N'-Dioctyl urea (C ₈ H ₁₇ NH) ₂ CO	90·0	89-90 ⁸	C = 72·14 H = 12·29 N = 9·78	C = 71·76 H = 12·76 N = 9·85
N, N'-Didecyl urea (C ₁₀ H ₂₁ NH) ₂ CO	95·0	95-97 ⁸ 94-95 ⁹	C = 73·58 H = 12·72 N = 8·03	C = 74·03 H = 12·9 N = 8·2
<i>n</i> -Heptyl ammonium <i>n</i> -Heptyl carbamate (C ₇ H ₁₅ NH CO NH ₃ C ₇ H ₁₅)	82·0	82-84 ¹⁰	C = 65·92 H = 12·87 N = 10·59	C = 65·64 H = 12·48 N = 10·21
<i>n</i> -Octyl ammonium <i>n</i> -Octyl carbamate (C ₈ H ₁₇ NH CO NH ₃ C ₈ H ₁₇)	86·0	84-86 ¹⁰	C = 67·53 H = 13·11 N = 9·57	C = 67·48 H = 12·66 N = 9·26
<i>n</i> -Decyl ammonium <i>n</i> -decyl carbamate (C ₁₀ H ₂₁ NH CO NH ₃ C ₁₀ H ₂₁)	89·0	90·0 ¹¹	C = 70·41 H = 12·88 N = 7·9	C = 70·33 H = 12·92 N = 7·81

N.B.—Superscripts indicate the reference numbers.

TABLE II

Heats of combustion of substituted ureas and carbamates referring to the solid state at 25° C.

Substance	$-\Delta E_s^\circ$ cal./g. (Mean)	$-\Delta E_s^\circ$ K.cal. mole ⁻¹ (25° C.) (Mean)	$-\Delta H_s^\circ$ K.cal. mole ⁻¹ (25° C. and 1 atm.) (Mean)	Increase in the heat of combustion per CH ₂ group K.cal. mole ⁻¹	$-\Delta H_f^\circ$ of the compound K.cal. mole ⁻¹ (25° C. and 1 atm.)
1. N, N'-Diheptyl urea	9164±5	2350±1.3	2353±1.3	152.3	150.0
2. N, N'-Dioctyl urea (Com- pound 1 + 2 CH ₂)	9326±4	2654±1.1	2658.4±1.1	152.5	170.2
3. N, N'-Didecyl urea (Com- pound 2 + 4 CH ₂)	9579±5	3263±1.7	3268.5±1.7		209.4
4. <i>n</i> -Heptyl ammonium <i>n</i> -heptyl carbamate	8549±6	2346±1.6	2349.8±1.6	152.3	222.2
5. <i>n</i> -Octylammo- nium <i>n</i> -octyl carbamate (compound 4 + 2 CH ₂)	8758±4	2650±1.2	2654.4±1.2	152.5	242.5
6. <i>n</i> -Decyl ammo- nium <i>n</i> -decyl carbamate (compound 5 + 4 CH ₂)	9088±5	3259±1.8	3264.6±1.8		282.8
				Mean = 152.4	

N.B.—The uncertainties given in Table II are the average deviations of the mean.

CONCLUSION

It is seen from Table II that the average increase in the heat of combustion, ΔH_c° , per CH_2 group in the hydrocarbon chain of the urea derivatives and the respective carbamates is 152.4 K.cals. corresponding to the value of 156.3^{11} K.cals. observed in the homologous series of paraffin hydrocarbons. Since the increase in the heat of combustion per CH_2 group has attained a constant value of 152.4 K.cals, data for the heats of combustion of the higher substituted ureas and carbamates could be obtained by the addition of the proper multiple of the above value to the heat of combustion of the preceding compound.

REFERENCES

1. *Manual No. 117, Parr Oxygen Bomb Calorimeters*, Parr Instrument Company, Illinois.
2. *A.S.T.M. Standards*, 1949, Part 5, p. 605.
3. Dickinson, H. C. .. *Bull. Natl. Bur. Standards*, 1915, **11**, 189.
4. Venugopala Charlu, T. .. "Studies on high pressure reactions, (a) Aliphatic amines and carbon dioxide, (b) 1-4 dioxane, carbon monoxide and water," *Ph.D. Thesis*, Indian Institute of Science, Bangalore, 1962.
5. Moore, M. B. and Wright, H. B. .. *J. Am. Chem. Soc.*, 1948, **70**, 3865.
6. *Org. Reactions*, Ed. Roger Adams *et al.*, John Wiley and Sons, Inc., 1947, **3**, 307.
7. Chabrier, P. and Najer, H. .. *Bull. Soc. Chim. France*, 1957, **2**, 1069-072.
8. Fred Applegath *et al.* .. *Brit. Pat.* 818,864 (To Monsanto Chemical Co.), 26 Aug. 1959; *Chem. Abstr.*, 1960, **54**, 9774.
9. Scott, F. L. and Scott, M. T. .. *J. Am. Chem. Soc.*, 1957, **79**, 6081.
10. Hunter, B. A. and Glenn, H. D. .. *U.S. Pat.* 2,635,124 (To United States Rubber Co.), April 14, 1953; *Chem. Abstr.*, 1953, **47**, 7814.
11. Leibnitz, E. *et al.*; .. *Chem. Abstr.*, 1961, **55**, 365.
12. Lange, N. A. .. *Handbook of Chemistry*, McGraw-Hill Book Co., Inc., New York, 1956.
13. Prosen, E. J. and Rossini, F. D. .. *J. Research, Natl. Bur. Standards*, 1945, **34**, 263.