Thermochimica Acta, 126 (1988) 13–16
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

HYDROACRIDINES. XII. THERMOCHEMICAL CHARACTERIZATION OF 4aα,8aβ,9aβ,10aα- and 4aα,8aβ,9aα,10aα-TETRADECAHYDROACRIDINE

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(Received 28 April 1987)

ABSTRACT

The heats of combustion of 4aα,8aβ,9aβ,10aα-tetradecahydroacridine (α-perhydroacridine, I) and 4aα,8aβ,9aα,10aα-tetradecahydroacridine (β-perhydroacridine, II) were determined, and the standard heats of formation ($\Delta H_f^{\ominus}$) were deduced therefrom: -62.90 ± 0.57 for I and -60.38 ± 0.59 kcal mol^{-1} for II. These experimental results are in very good agreement with the values estimated theoretically for each of the compounds.

INTRODUCTION

In the previous papers in this series, the syntheses and NMR-structural analyses of three stereoisomeric perhydroacridines and a larger number of their derivatives were reported [1]. Recently we started to study these compounds further by thermochemical methods.

In this paper we report the results of the determination of the heats of combustion and the calculation of the heats of formation for two of the parent compounds: α-perhydroacridine and β-perhydroacridine. A comparison is also made with their carbocyclic analogues, the corresponding stereoisomeric perhydroanthracenes.

EXPERIMENTAL

The synthesis, separation and purification of the stereoisomeric perhydroacridines I and II were described in an earlier paper [2].

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0040-6031/88/$03.50

Prior to combustion, the samples were dried in the desiccator, and then pressed into 0.3–0.36 g pellets and weighed to 0.01 mg. A CB-100-type Gallenkamp, adiabatic bomb of 0.3 l capacity, containing a pellet and 1.00 g water was flushed twice at 20 atm of oxygen, then charged to 30 atm with oxygen at 25.0 °C. Ignition was achieved using a cotton thread lit by a chromium–nickel wire, for both of which the thermochemical characteristics were known [3]. The caloric capacity of the system was evaluated in calibration experiments with benzoic acid [4,5].

The calorimetric system was equipped with a mercury thermometer calibrated to 0.01 K, and an auxiliary optic dispozitive, allowing accuracy of 0.002–0.001 K.

Three combustion runs were carried out for each stereoisomer. In no run was the presence of carbon detected.

RESULTS AND DISCUSSION

From the equation of combustion of perhydroacridine

$$C_{13}H_{23}N(s) + \tfrac{37.5}{2}O_2(g) \rightarrow 13CO_2(g) + \tfrac{23}{2}H_2O(l) + \tfrac{1}{2}N_2(g)$$

the heat of formation was deduced by means of the relation

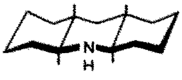
$$\Delta H_f^{\ominus} = -\Delta H_c^{\ominus} - 13\Delta H_f,\ CO_2(g) - \tfrac{23}{2}\Delta H_f,\ H_2O(l)$$

where ΔH_f, $CO_2(g)$ and ΔH_f, $H_2O(l)$ are the known heats of formation [6] of carbon dioxide and water, respectively.

The experimental results for the heats of combustion of α- (**I**) and β-perhydroacridine (**II**) are listed in Tables 1 and 2, respectively.

We attempted to evaluate the heats of formation of α- and β-perhydroacridine from the known heats of formation of cyclohexane (**III**) [7], piperidine (**IV**) [8] and 4aα,8aβ,9aβ,10aα-tetradecahydroanthracene (*trans,syn, trans*-perhydroanthracene, **V**) [9], assuming that replacement of a $-CH_2-$ group by a –NH– group, both in cyclohexane and perhydroanthracene, had to produce the same change in the heats of formation, $\Delta(\Delta H_f^{\ominus})$ (see Table 3).

The value of -62.95 kcal mol^{-1} which was found for α-perhydroacridine is in excellent agreement with the value of -62.90 ± 0.57 kcal mol^{-1} obtained from the heat of combustion.



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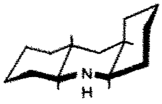


II

TABLE 1

Experimental results for the determination of the heat of combustion of α-perhydroacridine

	Run		
	1	2	3
Amount of sample (g)	0.32624	0.35642	0.34723
Amount of water (g)	1	1	1
Heat of ignition (cal) [a]	28.9	25.3	28.9
$q\mathrm{HNO_3}$ (cal)	6.2	6.2	6.2
ΔT (K)	1.259	1.372	1.341
$-\Delta U_c^{\ominus}$(298.15 K) (kcal mol^{-1})	1942.31	1940.74	1944.91
$-\Delta H_c^{\ominus}$(298.15 K) (kcal mol^{-1})	1945.42	1943.85	1947.02

[a] Combustion of the cotton thread and the chromium–nickel wire. Average $\Delta H_c^{\ominus} = -1945.43$ kcal mol^{-1}; average $\Delta H_f^{\ominus}$[**I**(s)] $= -62.90 \pm 0.57$ kcal mol^{-1}.

TABLE 2

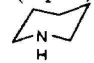
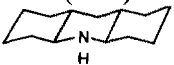
Experimental results for the determination of the heat of combustion of β-perhydroacridine

	Run		
	1	2	3
Amount of sample (g)	0.30741	0.31668	0.32607
Amount of water (g)	1	1	1
Heat of ignition (cal) [a]	26.2	24.9	28.9
$q\mathrm{HNO_3}$(cal)	6.2	6.2	6.2
ΔT (K)	1.188	1.222	1.260
$-\Delta U_c^{\ominus}$(298.15 K) (kcal mol^{-1})	1944.83	1943.24	1946.42
$-\Delta H_c^{\ominus}$(298.15 K) (kcal mol^{-1})	1947.94	1946.35	1949.53

[a] Combustion of the cotton thread and the chromium–nickel wire. Average $\Delta H_c^{\ominus} = -1947.94$ kcal mol^{-1}; average $\Delta H_f^{\ominus}$[**II**(s)] $= -60.38 \pm 0.59$ kcal mol^{-1}.

TABLE 3

Evaluation of the standard heat of formation of α-perhydroacridine, from the heats of formation of cyclohexane, piperidine and *trans,syn,trans*-perhydroanthracene

Compound	$\Delta H_f^{\ominus}$ (kcal mol^{-1})	Ref.	Compound	$\Delta H_f^{\ominus}$ (kcal mol^{-1})	Ref.
 **III**(liquid)	-37.40	7	 **V**(solid)	-79.21	9
 **IV**(liquid)	-21.15	8	 **I**(solid)	-62.96 (calculated)	–
	$\Delta(\Delta H_f^{\ominus}) = -16.25$			$\Delta(\Delta H_f^{\ominus}) = -16.25$	

The heat of formation of β-perhydroacridine (in this molecule there are three gauche interactions) is determined by adding 2.4 kcal mol^{-1} (0.8 kcal mol^{-1} for each gauche interaction [10]) to the heat of formation of α-perhydroacridine. So the value -60.56 kcal mol^{-1} is obtained, which also agrees very well with our experimental value of -60.38 ± 0.59 kcal mol^{-1}.

Calculation of the heat of combustion using the method of group contributions of Handrick [11], which does not take into account energy differences within stereoisomers, gives $\Delta H_c^{\ominus} = -1942.35$ and $\Delta H_f^{\ominus} = -65.98$ kcal mol^{-1} for perhydroacridine * which, although very satisfactory, are obviously less accurate than the values reached by the former method.

The heat of formation $\Delta H_f^{\ominus} = -62.90$ kcal mol^{-1} obtained for α-perhydroacridine is also very well confirmed by using it, with the heat of formation of acridine ($\Delta H_f^{\ominus} = +48.0$ kcal mol^{-1} [12]), for calculation of the heat of hydrogenation of acridine to α-perhydroacridine. The resulting value of 110.90 kcal mol^{-1} is, as expected, very close to 110.08 kcal mol^{-1}, which is the heat of hydrogenation of anthracene ($\Delta H_f^{\ominus} = +30.87$ kcal mol^{-1} [13]) to the perhydroanthracene V ($\Delta H_f^{\ominus} = -79.21$ kcal mol^{-1} [9]), as calculated from their heats of formation.

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* These values, however, have to be assigned to α-perhydroacridine, the most strainless of all possible stereoisomers.