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THERMAL STUDIES OF POLYNITROBISHOMOCUBANES

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ABSTRACT

A series of polynitrobishomocubanes as well as other substituted bishomocubanes has been thermally characterized by differential scanning calorimetry. The results indicate that these polynitropolycyclic cage compounds have high thermal stabilities relative to the parent hydrocarbon, 1,3-bishomocubane, and comparable thermal stabilities to bishomocubanes containing substituents other than the nitro group. In addition the apparent activation energy for the thermal decomposition of 5,5-dinitropentacyclo[5.3.0.0^{2,6}.0^{3,10}.0^{4,8}]decane-3-carboxylic acid has been determined to be in the range 202–210 kJ mol^{-1}.

INTRODUCTION

Recent efforts in several laboratories have been directed toward the synthesis and thermal characterization of polynitropolycyclic "cage" compounds (e.g., cubanes, bishomocubanes, homocubanes and adamantane derivatives) [1–4]. The more highly strained polynitro members of this group are predicted to comprise a new class of high-density energetic materials based on thermohydrodynamic calculations [5–7]. In the present work, a series of bishomocubane derivatives has been studied by differential scanning calorimetry (DSC) with the goal of determining thermal stabilities. This ring system is the first strained polycyclic system to contain at least four nitro groups; hence, the results of the study should afford information pertaining to the relative stabilities of strained polynitro cage systems.

EXPERIMENTAL

Differential scanning calorimetry runs were made on a Perkin-Elmer DSC-4/TADS system operated in the heating mode at a sensitivity of 2

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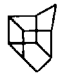
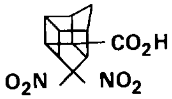
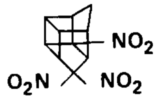
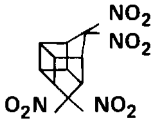
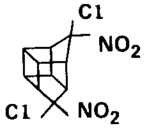
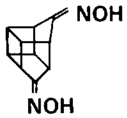
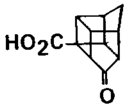
TABLE 1

Thermal properties of pentacyclo[5.3.0.0^{2,6}.0^{3,10}.0^{4,8}]decanes [a]

Compound		Transition temp. (T_t, °C)	Melting temp. (T_m, °C)	Decomposition temp. (T_d, °C)
	**1** [f]	[b]	138.6	168
	**2** [g]	[c]	137.2	268
	**3** [g]	66.9	201.1	291
	**4** [h]	97.9	147.5	279
	**5** [e,h]	[b]	[d]	267
	**6** [e,h]	[b]	[d]	262
	**7** [g]	[b]	69.5	282

[a] Heating rate = 10°C min^{-1}.

[b] No transition in the range −30°C to melting point.

[c] No transition in the range 50°C to melting point.

[d] Decomposition occurs on melting.

[e] Mixture of isomers.

[f] Synthesis, see ref. 7a.

[g] Synthesis, see ref. 3.

[h] Synthesis, see ref. 4.

mcal s^{-1} at full-scale deflection. The heating rate for all runs was 10°C min^{-1} (Table 1). Samples were contained in re-usable stainless-steel, high-pressure cells; sample quantities were typically ca. 1 mg. Reported temperatures are mean values of at least three runs corrected to an indium standard with estmated errors in the decomposition temperatures (T_d, Table 1) of ± 2°C. Kinetic determinations were made by using the same pans; the data were analyzed according to the methods described by Kissinger [8] and by Ozawa [9].

RESULTS

The results of the study are given in Table 1. Due to the high symmetry and globular molecular shape of the bishomocubane cage, some of the compounds have been found to possess an orientationally disordered solid phase. Such behavior is common in other quasi-spherical cage compounds (e.g., camphor, norbornane, and adamantane) [10]. The data presented in column 1 of the table show that these compounds undergo a solid-state phase transition prior to melting with a low entropy of fusion. For these compounds, ΔS_f is typically less than 20 J mol^{-1} K^{-1}, a value that is indicative of a high degree of motional freedom in the solid state [11]. Pentacyclo[5.3.0.0^{2,6}.0^{3,10}.0^{4,8}]decane (1,3-bishomocubane, **1**) as well as the corresponding trinitro- and tetranitro-1,3-bishomocubanes (**3** and **4**, respectively) exhibit this type of thermal behavior; their respective entropies of fusion are 10.6, 6.3, and 5.0 J mol^{-1} K^{-1}. This behavior stands in contrast with that of 5,5-dinitropentacyclo[5.3.0.0^{2,6}.0^{3,10}.0^{4,8}]decane-3-carboxylic acid, **2**, which is a brittle solid that possesses an entropy of fusion of 27 J mol^{-1} K^{-1}.

Table 1 also shows that the four polynitro-1,3-bishomocubanes have high thermal stabilities relative to the parent hydrocarbon, **1**. In addition their thermal stabilities are comparable to that of the corresponding non-NO_2-containing ketoacid, **7**. An increase in the decomposition temperature of the substituted compounds compared to 1,3-bishomocubane is partially explained by their higher melting points, since many organic compounds (e.g., HMX and RDX) are known to be catalytically decomposed by the liquid phase [12]. However, while the melting points of **1**, **2**, and **4** are comparable, the decomposition temperature, T_d, of 1,3-bishomocubane is ca. 100–110°C lower than that of the two substituted compounds. Thus, intermolecular ordering forces seem to be important in stabilizing the liquid phases of **2**, **3**, **4**, and **7** relative to that of **1** (which decomposes shortly after melting).

The lower exotherm onset of **2** vis-a-vis **3** is a trend that has also been observed in carboxy-substituted cubanes [13]. In carboxy-substituted cubanes, the biradical formed via cleavage of a ring carbon–carbon bond appears to be stabilized by the cumulative inductive effects of substituents on the cage system. This behavior has also been observed in substituted diazenes [14]. In addition it should be recognized that decarboxylation is a viable decomposition pathway for carboxy-substituted compounds.

A kinetic study on compound **2** was conducted to determine the activation energy for thermal decomposition. The kinetic methods employed, i.e., those of Kissinger [8] and of Ozawa [9], are similar in that the temperature that corresponds to a peak maximum is studied as a function of the scanning rate of the instrument. Historically, these methods have come under criticism when applied to complex solid-state decompositions (e.g., nitramine decompositions). However, thermally induced bond breaking in cubane has been shown to afford relatively few fragments [15]. Results of theoretical calculations [16] indicate that cleavage of carbon–carbon framework bonds in strained nitro-substituted cages occurs prior to cleavage of C–NO_2 bonds. Thus, the likelihood of competing side reactions in the decomposition of nitro-substituted carbocyclic systems is small when compared with the decomposition behavior of the nitramines. Accordingly, the kinetics of decomposition of strained carbocyclic systems are expected to approach that of a truly first-order process [17]. This behavior is a necessary requirement for the rigorous application of the above kinetic treatments.

The apparent activation energy for the thermal decomposition of 5,5-dinitropentacyclo[5.3.0.0.^{2,6}.0^{3,10}.0^{4,8}]decane-3-carboxylic acid, **2**, is 202 kJ mol^{-1} (Kissinger method [8]) and 210 kJ mol^{-1} (Ozawa method [9]) with $\log A = 17.9$ s^{-1}. The high activation energy and large exothermic heat of decomposition ($\Delta H_d = -526 \pm 20$ kJ mol^{-1}) are consistent with a biradical process. The thermal decomposition of hexamethylprismane [18,19] is also believed to occur via a biradical intermediate since the concerted decomposition pathway is symmetry forbidden [20]. The magnitude of E_a is suggestive of high thermal stability in the cage system; however, the only other activation energy available for comparison is cubane ($E_a = 181$ kJ mol^{-1} [15]). While the comparison is not strictly valid due to the higher strain energy of cubane relative to bishomocubane, recent calculations on strained molecules have shown that the presence of NO_2 groups actually increases the cage carbon–carbon bond strength relative to that of the parent hydrocarbon [21].

CONCLUSIONS

The results of thermal studies on substituted bishomocubanes indicate that nitro group substitution increases the thermal stability of the cage system relative to that of the parent hydrocarbon, 1,3-bishomocubane. This conclusion is important in assessing the thermal stability of strained polynitropolycyclic systems.

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