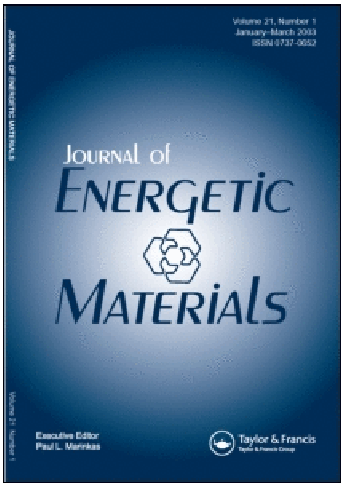

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THERMAL STUDIES OF 2-AZIDO-1,1-DINITROETHYL COMPOUNDS AND TRINITROMETHYL COMPOUNDS

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ABSTRACT

The thermal decomposition characteristics of 2-azido-1,1-dinitroethyl [-$C(NO_2)_2CH_2N_3$] compounds and trinitromethyl [-$C(NO_2)_3$] compounds have been studied by DTA, and their kinetic parameters are also reported. The results indicate that these 2-azido-1,1-dinitroethyl compounds have higher thermal stability relative to the corresponding trinitromethyl compounds.

INTRODUCTION

Recent efforts in several laboratories have been directed toward the synthesis and thermal characterization of organic azides, because they have many desirable features, such as high heat of formation, good thermal and hydrolytic

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stability, high burning rate, and reduced flash[1]

We have extended the research to the synthesis of the energetic 2-azido-1,1-dinitroethyl [-$C(NO_2)_2CH_2N_3$] derivatives[2]. It is a new class of azides and some of them derived directly from the corresponding trinitromethyl [-$C(NO_2)_3$] compound. Calculated heats of formation of this class of compounds indicated that a [-$C(NO_2)_2CH_2N_3$] compound should be obviously more energetic than its [-$C(NO_2)_3$] analogue[3]. Furthermore, since the dinitromethylene group has moderate energy and is among the most stable[4], a [-$C(NO_2)_2CH_2N_3$] should be more energetic and stable than its corresponding [-$C(NO_2)_3$] compound.

Hence, it occurred to us that it might be of interest to study their thermal stability. The results of the study should afford valuable information pertaining to the relative stability of the 2-azido-1,1-dinitroethyl compounds and the corresponding trinitromethyl compounds.

EXPERIMENTAL

Differential Thermal Analysis (DTA) was carried out from room temperature to 400℃ by using a PCR-1 DTA apparatus. 2 mg of sample synthesized by us was taken in an open Aluminum cup and heated at a rate of 2 ℃/min, 5 ℃/min, 10 ℃ /min and 20 ℃ /min, respectively in an atmosphere of static air, and the reproducibility of the results was satisfactory.

In order to calculate the kinetic parameters of the thermal decomposition, the peak maxima at various rates of heating were obtained at least two runs. The data were analyzed according to the methods described by Kissinger[5] and Ozawa[6].

RESULTS

The results given in Table 1, proved our supposition that [$-C(NO_2)_2CH_2N_3$] compounds possess higher thermal stability than the corresponding [$-C(NO_2)_3$] compounds. The decomposition temperatures (T_m) of the azides (**1, 3, 5, 7, 9**) are ca. 20 ℃ higher than that of the corresponding trinitromethyl analogues (**2, 4, 6, 8, 10**). The T_m of 1,4-bis (2-azido-1,1-dinitroethyl)benzene (**11**) and 1,3,5-tris(2-azido-1,1-dinitroethyl)benzene (**13**) are ca. 80 ℃ and 200 ℃ higher than that of trinitromethyl analogues **12** and **14**. Due to the replacement of one nitro of $-C(NO_2)_3$ by the azidomethyl group, the $C-NO_2$ rotational barrier would be substantially decrease, hence ease of bond breaking. Sensitivity would consequently be substantially decreased and the thermal stability would be increased. The decrease of the impact sensitivity also agrees well with this behavior. For example, $\overline{H_{50}}$ of 1,9-diazido-2,2,8,8-tetranitro-4,6-dioxa-nonane (**1**) is 45.5cm, and the corresponding trinitromethyl compound **2** is 24.6cm[2b].

The kinetic studies on the compounds were conducted to determine the activation energy for the thermal decomposition. The kinetic method employed, i.e., those of Kissinger[5] and of Ozawa[6], are similar in that the temperature, that corresponds to a peak maximum is studied as a function of the heating rate of instrument.

The activation energies for the thermal decomposition of azides (**1, 3, 5, 7, 9**) have been determined to be in the range of 125 ~ 225 kJ/mol, with *log*A=$7.14\times10^{13}\sim7.5\times10^{24}$ s^{-1}, and that of the corresponding trinitromethyl compounds (**2, 4, 6, 8, 10**) in the range of 107 ~ 176 kJ/mol, with *log*A=$6.2\times10^{11}\sim1.0\times10^{20}$ s^{-1}. The activation energies of 2-azido-1,1-dinitroethylbenzene derivatives **11** and **13** are 80 and 140 kJ/mol. That is to say the azides have higher activation energy than trinitromethyl analogues except compound 7.

CONCLUSION

The results of thermal studies indicate that the replacement of a $-NO_2$ group of $-C(NO_2)_3$ by $-CH_2N_3$ group may increase the thermal stability of the resulting compound. Since the 2-azido-1,1-dinitroethyl compounds possess high heat of formation (see Table 1), better thermal stability and lower impact sensitivity than that of the corresponding trinitromethyl compounds, they are promise as new energetic materials.

TABLE 1

The kinetic parameters of 2-azido-1,1-dinitroethyl compounds and trinitromethyl compounds

No.	Compounds	E kJ/mol	A s^{-1}	$k_{100°C}$ s^{-1}	T_m[a] °C	ΔH_f°[3] kJ/mol
1	$CH_2[OCH_2C(NO_2)_2CH_2N_3]_2$	145.40	1.80×10^{15}	7.96×10^{-6}	227.3	320.0 164.2[b]
2	$CH_2[OCH_2C(NO_2)_3]_2$	109.44	6.15×10^{11}	2.94×10^{-4}	204.9	-219.2
3	$CH_2[OCH_2CH_2C(NO_2)_2CH_2N_3]_2$				221.4	272.7
4	$CH_2[OCH_2CH_2C(NO_2)_3]_2$	107.63	7.96×10^{11}	6.82×10^{-4}	202.0	-226.9
5	$CH_3N(NO_2)CH_2C(NO_2)_2CH_2N_3$	148.31	5.50×10^{15}	9.53×10^{-6}	216.5	220.2
6	$CH_3N(NO_2)CH_2C(NO_2)_3$	131.48	1.06×10^{15}	4.17×10^{-4}	186.1	-49.6
7	$O_2NN[CH_2C(NO_2)_2CH_2N_3]_2$	125.08	7.14×10^{13}	2.21×10^{-4}	196.3	495.2 553.4[b]

8	$O_2NN[CH_2C(NO_2)_3]_2$	127.41	6.56×10^{14}	9.57×10^{-4}	175.5	-44.4 -28.0[9]
9	$[CH_2N(NO_2)CH_2C(NO_2)_2CH_2N_3]_2$	225.61	7.51×10^{24}	1.96×10^{-7}	203.5	483.6
10	$[CH_2N(NO_2)CH_2C(NO_2)_3]_2$	176.17	1.00×10^{20}	2.19×10^{-5}	189.6	-55.9
11	p-C_6H_4-$[C(NO_2)_2CH_2N_3]_2$	140.84	3.91×10^{16}	7.51×10^{-4}	206.1	678.7
12	p-C_6H_4-$[C(NO_2)_3]_2$[10]	109.40	8.71×10^{13}		129.7	72.9
13	m-C_6H_3-$[C(NO_2)_2CH_2N_3]_3$	82.72	4.68×10^{9}	1.23×10^{-2}	230.0	882.6
14	m-C_6H_3-$[C(NO_2)_3]_3$				<30	90.8

a. Heating rate=10℃/min.

b. Using the found value of the heat of combustion

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