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Enthalpies of Combustion, Vaporization, and Formation of 3,3,4,4-Tetramethyl-Δ^1-1,2-diazetine and Di-*tert*-butyldiazene

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Measurements were made of the enthalpies of combustion of both compounds and of the vaporization of tetramethyldiazetine. Standard enthalpies of formation were calculated as follows, in kcal mol⁻¹: for tetramethyldiazetine, crystal +21.04 ± 0.64, gas +35.92 ± 0.69; for di-*tert*-butyldiazene, liquid −18.04 ± 0.65, gas −8.70 ± 0.66.

1. Introduction

This investigation was carried out to determine the enthalpy of formation of 3,3,4,4-tetramethyl-Δ^1-1,2-diazetine, which has the structure
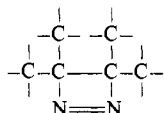
and to confirm a previous measurement of the enthalpy of combustion of di-*tert*-butyldiazene, which has the structure
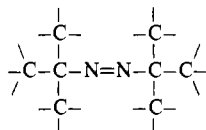
Data on the cyclic diazene are important in connection with the problem of the decomposition of cyclic alkyldiazenes.

The combustion experiments were performed in the Thermochemical Laboratory at Rice University and the vaporization experiments at the University of Lund.

The values of the atomic weights used were as follows (1): C, 12.011; H, 1.0079; N, 14.0067. These yield the following atomic weights: tetramethyldiazetine, $C_6H_{12}N_2$, 112.1742; di-*tert*-butyldiazene, $C_8H_{18}N_2$, 142.2436.

2. Experimental Section

Materials. The synthesis and purification of the di-*tert*-butyldiazene are described in ref 3. Analysis by gas chromatography of this sample of di-*tert*-butyldiazine indicated the following impurities, in weight percent: isobutene, 0.016; isobutane, 0.018; *n*-pentane, 0.013; 2-methylpentane (?), 0.005; 2-methylbutane (?), 0.003.

The synthesis and purification of the tetramethyldiazetine is described by Engel, Hayes, Keifer, Szilagyi, and Timberlake (2). Analysis by flame ionization gas chromatography of this sample of tetramethyldiazetine indicated no detectable impurities, with an apparatus having a sensitivity of better than 0.10%.

Enthalpy of Combustion. The calorimetric apparatus used was that assembled by Margrave (6) and associates. Except as otherwise noted, all procedures, details of operations, calculations, etc., were carried out as previously reported (3, 4). For these combustion experiments, the samples were placed in polyester (Mylar) bags, as previously described (3).

Table I. Results of Five Experiments on the Combustion of Tetramethyldiazetine (Solid) at 298.15 K

m_{sample}/g	$10^5 k/s^{-1}$	$10^4 u/K\ min^{-1}$	$\Delta t/K$	$\Delta t_c/K$	$\epsilon/J\ K^{-1}$	q_m/J	q_n/J	q_i/J	$-\Delta E_c/kJ\ mol^{-1}$
0.39224–0.49768	3.22–3.31	0.91–1.34	1.0219–1.3145	1.01805–1.30857	15261.21–15261.45	852.48–1402.98	40.74–51.13	70.45–81.88	4158.14–4162.43
0.46055[a]			1.1974[a]	1.19228[a]	15261.37[a]	994.73[a]	46.24[a]	73.96[a]	4160.43[a,b]

[a] Mean value. [b] Standard deviation of the mean: ±0.87.

Table II. Results of Six Experiments on the Combustion of Di-tert-butyldiazene (Liquid) at 298.15 K

m_{sample}/g	$10^5 k/s^{-1}$	$10^4 u/K\ min^{-1}$	$\Delta t/K$	$\Delta t_c/K$	$\epsilon/J\ K^{-1}$	q_m/J	q_n/J	q_{im}/J	q_i/J	$-\Delta E_c/kJ\ mol^{-1}$
0.55050–0.72292	3.35–3.46	0.74–3.68	1.5399–1.9877	1.53045–1.97938	15261.37–15261.96	1316.22–1544.83	50.32–56.61	2.65–3.48	74.20–75.67	5636.81–5639.37
0.63378[a]			1.7556[a]	1.74810[a]	15261.66[a]	1426.43[a]	53.97[a]	3.05[a]	74.98[a]	5637.96[a,b]

[a] Mean value. [b] Standard deviation of the mean: ±0.34.

The energy equivalent of the standard calorimeter system was determined using standard benzoic acid, National Bureau of Standards No. 39i, which was certified to have a specific energy of combustion at 298.15 K of (26434 ± 3) J g^{-1} under the specified conditions. The present measurements were performed during the same period of time as the experiments on three hydrocarbons previously reported (7) and the same value of the energy equivalent of the standard calorimeter system was used, namely, 15241.43 J K^{-1}, with a standard deviation of ±0.93 J K^{-1}. The details are given in Table I of ref 7.

In the combustion experiments on the di-*tert*-butyldiazene the fuse wire burned completely in all six of these experiments. No soot and no significant carbon monoxide were found in these experiments. One experiment was discarded because, for some unknown reason, its value was more than six times the standard deviation away from the mean.

In the combustion experiments on the tetramethyldiazetine, the fuse wire burned completely in two of the five experiments. Traces of soot were noted in four of these experiments, but the amounts of carbon monoxide were not significant. In two other experiments, large amounts of soot and carbon monoxide were found and these two experiments were discarded. Additional experiments were not possible because of the limited quantity of material.

The quantity of reaction in the combustion experiments was determined from the mass of sample placed in the bomb.

The results of the combustion experiments are given in Tables I and II. The symbols used are the same as in the preceding reports (*3*, *4*, *7*).

Table I gives the results of five experiments on the calorimetric combustion of tetramethyldiazetine.

Table II gives the results of six experiments on the calorimetric combustion of di-*tert*-butyldiazene. Correction for the observed impurities in this sample was made as indicated in the column labeled g_{im}.

Table III gives the values for ΔE_c, $\Delta E_c{}^\circ$, and $\Delta H_c{}^\circ$. The overall uncertainty assigned to the value of $\Delta H_c{}^\circ$ in the last column is twice the overall propagated standard deviation of the mean, covering the following components: for the certified value of the energy of combustion of standard benzoic acid; for the measured value of the energy equivalent of the standard calorimeter system; for the combustion experiments on the two compounds; and ±0.02% for the effects of the unknown impurities in the two compounds.

In Tables I and II, q_m is the energy of combustion of the polyester (Mylar) in the presence of the combustion products of the other material present. The value of q_m for each set of experimental conditions is calculated from data in ref 3 by applying the sums and differences of the appropriate Washburn corrections. The quantity, ΔE_c, thus represents the energy of the bomb process of combustion, fully corrected for all effects of the polyester (Mylar), including its effect on the Washburn correction. It should be noted that the form of presentation of the calorimetric data here follows the form used by Rossini (F.D.R.) over the years. This involves specific identification of the energy of the bomb process, followed by application of the Washburn correction and conversion to the standard enthalpy of combustion. This is a simple procedure when metal wire is used for ignition and glass bulbs used to contain the sample. However, when the material used for ignition, for containing the sample, and for an auxiliary combustible produces gaseous and/or liquid products of combustion, the procedure becomes more complicated. If one wishes, one may then, by a suitable calculation program, go directly to the standard enthalpy of combustion, omitting direct identification of the energy of the bomb process and its specific relation to the energy effects associated with ignition, sample container, and combustible material. We have chosen to perform further calculations (including some by hand) to separate and identify (a) the energy

Table III. Standard Energy and Enthalpy of Combustion of the Two Compounds at 298.15 K

| Compound | | | | $-\Delta E_c^\circ/kJ$ mol^{-1} | | |
Formula	Name	State	$-\Delta E_c/kJ$ mol^{-1}		$-\Delta H_c^\circ/kJ$ mol^{-1}	$-\Delta H_c^\circ/kcal_{th}$ mol^{-1}
$C_6H_{12}N_2$	Tetramethyl-diazetine	c	4160.43	4159.09	4164.05 ± 2.48	995.23 ± 0.59
$C_8H_{18}N_2$	Di-*tert*-butyldiazene	l	5637.96	5636.41	5645.09 ± 2.50	1349.21 ± 0.60

Table IV. Standard Enthalpies of Formation

| Compound | | | ΔH_f° (298.15 K) | |
Molecular formula	Name	State	kJ mol^{-1}	kcal$_{th}$ mol^{-1}
$C_6H_{12}N_2$	Tetramethyldiazetine [a]	c	+88.01 ± 2.69	+21.04 ± 0.64
		g	+150.26 ± 2.87	+35.92 ± 0.69
$C_8H_{18}N_2$	Di-*tert*-butyldiazene	l	−75.46 ± 2.74	−18.04 ± 0.65
		g	−36.38 ± 2.75	−8.70 ± 0.66

of the bomb process as if the sample container material were absent and (b) the total energy contribution from the sample container.

Enthalpy of Vaporization. The enthalpy of vaporization of liquid di-*tert*-butyldiazene was reported previously (*3*)

$$\Delta H_v^\circ(298.15 \text{ K}) = 39.08 \pm 0.25 \text{ kJ mol}^{-1} =$$
$$9.34 \pm 0.06 \text{ kcal}_{th} \text{ mol}^{-1}$$

For the measurements on tetramethyldiazetine, the Wadsö calorimeter was used, with the apparatus and procedure as described (*8*). Five experiments were performed, with a mean value of 62.25 kJ mol^{-1} and a standard deviation of the mean of ±0.27 kJ mol^{-1}. The overall uncertainty was taken as twice the standard deviation of the mean, plus an adequate allowance for possible uptake of water when filling the solid into the calorimeter under a stream of dry nitrogen. This gives for solid tetramethyldiazetine, at 298.15 K

$$\Delta H_v = \Delta H_v^\circ = 62.25 \pm 1.00 \text{ kJ mol}^{-1} =$$
$$14.88 \pm 0.24 \text{ kcal}_{th} \text{ mol}^{-1}$$

Previous Data. No previous measurements on the combustion or vaporization of tetramethyldiazetine have been reported.

Measurements on the combustion of di-*tert*-butyldiazene were reported from this laboratory in two previous investigations (*3*, *5*), for $-\Delta H_c^\circ$ at 298.15 K in kcal$_{th}$ mol^{-1}: from ref 5 in 1974, 1348.23 ± 0.39; from ref 3 in 1976, 1349.20 ± 0.85 (the original reported result has been corrected for an arithmetical error of 0.013%). The new value, 1349.21 ± 0.60, is in good accord with the more recent result.

Standard Enthalpies of Formation. Table IV gives the values of the standard enthalpies of formation for the two compounds,

in the condensed and gaseous states, as derived from the present data.

Discussion. The result from the present investigation on tetramethyldiazetine is being used by P.S.E. on the problem of the decomposition of cyclic azoalkanes and the result on di-*tert*-butyldiazene is being used by R.L.M. and F.D.R. on developing equations for calculating the enthalpies of formation of alkyldiazenes.

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