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Enthalpies of Combustion, Vaporization, and Formation of Phenylbenzene, Cyclohexylbenzene, and Cyclohexylcyclohexane; Enthalpy of Hydrogenation of Certain Aromatic Systems

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The enthalpies of combustion and vaporization were measured. Standard enthalpies of formation at 298.15 K were calculated as follows, in kcal_{th} mol⁻¹: for phenylbenzene, crystal 23.12 ± 0.62, hypothetical liquid 27.10 ± 0.63, gas 42.66 ± 0.62; for phenylcyclohexane, liquid -18.9 ± 1.34, gas -4.60 ± 1.35; for cyclohexylcyclohexane, liquid -66.05 ± 0.74, gas -52.19 ± 0.74. Analysis of these and earlier data shows that, within the assigned limits of uncertainty, the standard enthalpy of complete hydrogenation, in the gaseous state at 298.15 K, may be taken as (-15.88 ± 0.13) kcal_{th}/mol of H₂, for the following aromatic systems: naphthalene, phenylbenzene, phenylcyclohexane, and *n*-butylbenzene. This quantity may be useful in helping to estimate the enthalpy of hydrogenation of coal.

1. Introduction

This investigation is an extension of the experimental work on the relation between energy and molecular structure of hydrocarbons in which the senior author (F.D.R.) has been engaged for many years (20). With the availability of highly purified samples of phenylbenzene (diphenyl), cyclohexylbenzene (phenylcyclohexane), and cyclohexylcyclohexane (bicyclohexyl), it seemed desirable to confirm previously reported values of their standard enthalpies of combustion and obtain new values of their enthalpies of vaporization. Also, by having measurements on all three compounds made at the same time, in the same laboratory, by one investigator, and thus eliminating unknown systematic errors between them, one can obtain reliable values

of the relevant enthalpies of hydrogenation for both the gaseous and liquid states.

The combustion experiments on the three compounds 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 (6): C, 12.011; H, 1.0079. These yield the following molecular weights: phenylbenzene, C₁₂H₁₀, 154.2110; cyclohexylbenzene, C₁₂H₁₈, 160.2584; cyclohexylcyclohexane, C₁₂H₂₂, 166.3058.

2. Experimental Section

Materials. The materials used were American Petroleum Institute standard samples (purchased from the American Petroleum Institute Office of Standard Reference Materials, Carnegie-Mellon University, Pittsburgh, Pa.) having certified mole percentage impurities as follows: phenylbenzene, 0.02 ± 0.02; cyclohexylbenzene, 0.07 ± 0.05; cyclohexylcyclohexane, 0.023 ± 0.008.

Enthalpy of Combustion. The apparatus and procedures used in these experiments were essentially as previously reported (7, 8), with the bomb combustion apparatus having been assembled by Margrave and associates (10). The symbols used are the same as in the preceding reports (7, 8).

Fuse wire, Chromel C, was used as in the preceding investigation (8). The values used for determining the energy of ignition and the energy of combustion of the polyester (Mylar) were the same as before (8). The value used for the polyester (Mylar) was checked, satisfactorily, by a single experiment, in which enough polyester (Mylar) was burned to produce a temperature rise near 2 K.

Table I. Results of Five Experiments to Determine ϵ_s , the Energy Equivalent of the Standard Calorimeter System at 298.15 K

| m_{BA}/g | $10^3 k/s^{-1}$ | $10^4 u/K$ min^{-1} | $\Delta t/K$ | $\Delta t_c/K$ | $\Delta \epsilon/J K^{-1}$ | q_n/J | q_i/J | $\epsilon_s/J K^{-1}$ |
|----------------------|-----------------|--------------------------|---------------------|----------------------|----------------------------|-------------------|--------------------|-------------------------|
| 1.14659-1.16788 | 3.32-3.59 | 0.93-4.47 | 1.9993-2.0372 | 1.99105-2.02800 | 19.37-19.40 | 3.36-4.07 | 59.49-76.78 | 15238.36-15243.26 |
| 1.15669 ^a | | | 2.0176 ^a | 2.00857 ^a | 19.38 ^a | 3.64 ^a | 72.12 ^a | 15241.43 ^{a,b} |

^a Mean value. ^b Standard deviation of the mean: ±0.93.

Table II. Results of Seven Experiments on the Combustion of Phenylbenzene (Solid) at 298.15 K

| $m_{\text{sample}}/\text{g}$ | $10^3 k/\text{s}^{-1}$ | $10^4 u/\text{K min}^{-1}$ | $\Delta t/\text{K}$ | $\Delta t_c/\text{K}$ | $\epsilon/\text{J K}^{-1}$ | q_m/J | q_n/J | q_l/J | $-\Delta E_c/\text{kJ mol}^{-1}$ |
|------------------------------|------------------------|----------------------------|---------------------|-----------------------|----------------------------|---------------------|-------------------|--------------------|----------------------------------|
| 0.74005-0.81179 | 3.32-3.34 | 0.25-0.98 | 2.0338-2.2214 | 2.02736-2.21366 | 15260.40-15260.48 | 828.34-984.78 | 1.60-5.43 | 69.57-75.90 | 6243.02-6248.43 |
| 0.76862 ^a | | | 2.1114 ^a | 2.10386 ^a | 15260.43 ^a | 899.66 ^a | 3.79 ^a | 73.65 ^a | 6245.45 ^{a,b} |

^a Mean value. ^b Standard deviation of the mean: ± 0.69 .

Table III. Results of Six Experiments on the Combustion of Cyclohexylbenzene (Liquid) at 298.15 K

| $m_{\text{sample}}/\text{g}$ | $10^3 k/\text{s}^{-1}$ | $10^4 u/\text{K min}^{-1}$ | $\Delta t/\text{K}$ | $\Delta t_c/\text{K}$ | $\epsilon/\text{J K}^{-1}$ | q_m/J | q_n/J | q_l/J | $-\Delta E_c/\text{kJ mol}^{-1}$ |
|------------------------------|------------------------|----------------------------|---------------------|-----------------------|----------------------------|----------------------------|-------------------------|--------------------|----------------------------------|
| 0.61433-0.83575 | 3.27-3.35 | 1.06-3.11 | 1.7521-2.4730 | 1.74339-2.46434 | 15260.30-15260.53 | 0.00 ^a -1472.22 | 0.00 ^a -1.49 | 65.06-74.79 | 6919.66-6925.80 |
| 0.74340 ^b | | | 2.1650 ^b | 2.14628 ^b | 15260.44 ^b | 720.83 ^b | 0.68 ^b | 71.78 ^b | 6922.73 ^{b,c} |

^a Zero in the experiments using glass bulbs to contain the cyclohexylbenzene. ^b Mean value. ^c Standard deviation of the mean: ± 1.06 .

Table IV. Results of Eight Measurements on the Combustion of Cyclohexylcyclohexane (Liquid) at 298.15 K

| $m_{\text{sample}}/\text{g}$ | $10^3 k/\text{s}^{-1}$ | $10^4 u/\text{K min}^{-1}$ | $\Delta t/\text{K}$ | $\Delta t_c/\text{K}$ | $\epsilon/\text{J K}^{-1}$ | q_m/J | q_n/J | q_l/J | $-\Delta E_c/\text{kJ mol}^{-1}$ |
|------------------------------|------------------------|----------------------------|---------------------|-----------------------|----------------------------|----------------------|-------------------|--------------------|----------------------------------|
| 0.63363-0.88606 | 3.30-3.38 | 0.07-1.11 | 1.9998-2.7492 | 1.99302-2.73960 | 15260.28-15260.59 | 1325.03-1461.05 | 1.07-1.61 | 66.64-75.20 | 7575.18-7581.78 |
| 0.77099 ^a | | | 2.4068 ^a | 2.39885 ^a | 15260.45 ^a | 1398.77 ^a | 1.30 ^a | 72.02 ^a | 7578.83 ^{a,b} |

^a Mean value. ^b Standard deviation of the mean: ± 0.91 .

The procedure and values for correcting for the nitric acid formed in the combustion were the same as in a preceding report (7).

The energy equivalent of the standard calorimeter system was determined using standard benzoic acid, National Bureau of Standards No. 391, which was certified to have a specific energy of combustion at 298.15 K of $(26434 \pm 3) \text{ J g}^{-1}$ under the specified conditions.

The amount of reaction in each experiment was determined from the mass of sample placed in the bomb, with the balance, calibration, and procedure of weighing as previously described. All weights were reduced to vacuum.

The gaseous products of combustion were tested for carbon monoxide after each experiment, as previously described (7, 8), with no significant amount of it being found in any experiment.

The bomb was purged with oxygen gas by filling it to a pressure of about 3.45 MPa (about 34 atm gauge) and then releasing it to the atmosphere. In some experiments, the purge was performed near atmospheric pressure with a steady flow of oxygen (about 0.4 L min^{-1}) through the bomb for 5 min. This latter procedure minimized disturbance of the samples by changes in pressure as well as reducing the amount of nitric acid formed in the combustion. No systematic difference in the experimental results was noted between the two purging methods, and calculations made by assuming complete saturation of the oxygen with water vapor indicated no significant amount of water lost.

The phenylbenzene was transferred from its original container (Pyrex glass, sealed "in vacuo") in an atmosphere of dry nitrogen, pressed into pellets, and then stored in a desiccator protected with magnesium perchlorate. For each combustion experiment with this material, one pellet was sealed in a polyester (Mylar) bag.

The two liquid hydrocarbons, cyclohexylbenzene and cyclohexylcyclohexane, were initially planned to be placed in sealed glass bulbs for combustion (12), with the transfer from the original containers (Pyrex glass, sealed "in vacuo") being performed in an atmosphere of dry nitrogen. Practical difficulties in carrying out this procedure, arising from local conditions in the laboratory, resulted in consumption of excessive material for each successful experiment. Most of the combustion experiments on these two compounds were therefore performed with the liquid sealed in polyester (Mylar) bags.

The results of the combustion experiments are given in Tables I-IV. The symbols used are the same as in the preceding investigations (7, 8). In these tables 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 7 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.

Table I gives the results of five experiments, with standard benzoic acid, to determine the energy equivalent of the standard calorimeter system, ϵ_s . The fuse wire burned completely in four of the five experiments. This determination of ϵ_s was made during the period when the regular combustion experiments on the three hydrocarbons were being performed. This value of ϵ_s is in very good accord with the value from the previous investigation (8), $(15240.07 \pm 1.66) \text{ J K}^{-1}$, and with a value determined after the completion of the regular combustion experiments $(15242.31 \pm 0.94) \text{ J K}^{-1}$.

Table II gives the results of seven measurements on the calorimetric combustion of biphenyl. The fuse burned completely in four of the seven experiments.

Table III gives the results of six measurements on the calorimetric combustion of cyclohexylbenzene. Three of the

Table V. Standard Energy and Enthalpy of Combustion of the Three Hydrocarbons at 298.15 K

| Compound | | | $-\Delta E_c^\circ/\text{kJ mol}^{-1}$ | $-\Delta E_c^\circ/\text{kJ mol}^{-1}$ | $-\Delta H_c^\circ/\text{kJ mol}^{-1}$ |
|------------------------------|-----------------------|-------|--|--|--|
| Formula | Name | State | | | |
| $\text{C}_{12}\text{H}_{10}$ | Phenylbenzene | c | 6245.45 | 6241.82 | 6248.02 ± 2.07 |
| $\text{C}_{12}\text{H}_{16}$ | Cyclohexylbenzene | l | 6922.73 | 6919.66 | 6929.58 ± 5.39 |
| $\text{C}_{12}\text{H}_{22}$ | Cyclohexylcyclohexane | l | 7578.83 | 7576.27 | 7589.90 ± 2.62 |

Table VI. Results of the Vaporization Experiments

| Compound | | | Process | No. of experiments | ΔH_v | |
|-----------------------|------------------------------|-------|---------|--------------------|----------------------|---|
| Name | Formula | State | | | kJ mol^{-1} | $\text{kcal}_{\text{th}} \text{mol}^{-1}$ |
| Phenylbenzene | $\text{C}_{12}\text{H}_{10}$ | c | c → g | 6 | 81.75 ± 0.20 | 19.54 ± 0.05 |
| Cyclohexylbenzene | $\text{C}_{12}\text{H}_{16}$ | l | l → g | 5 | 59.94 ± 0.30 | 14.33 ± 0.07 |
| Cyclohexylcyclohexane | $\text{C}_{12}\text{H}_{22}$ | l | l → g | 5 | 57.98 ± 0.24 | 13.86 ± 0.06 |

Table VII. Comparison with Previous Data on Enthalpies of Combustion at 298.15 K

| Investigators | Phenylbenzene (c) $-\Delta H_c^\circ/\text{kcal}_{\text{th}} \text{mol}^{-1}$ | Cyclohexylbenzene (l) $-\Delta H_c^\circ/\text{kcal}_{\text{th}} \text{mol}^{-1}$ | Cyclohexylcyclohexane (l) $-\Delta H_c^\circ/\text{kcal}_{\text{th}} \text{mol}^{-1}$ |
|-------------------------------------|--|--|--|
| Stohmann, Kleber, and Langbein (23) | 1493.4 ± 1.5 | | |
| Barker (1) | 1500 ± 3 | | |
| Brüll (3) | 1493.8 ± 2.0 | | 1801.9 ± 2.0 |
| Parks and Vaughan (17) | 1493.30 ± 0.37 | | |
| Mackle and O'Hare (13) | 1493.35 ± 0.96 | | |
| Coleman and Pilcher (5) | 1494.22 ± 0.33 | | |
| Good and Lee (9) | | 1656.84 ± 0.22 | 1814.76 ± 0.24 |
| This report | 1493.31 ± 0.50 | 1656.21 ± 1.29 | 1814.03 ± 0.63 |

measurements were made using glass bulbs and three using polyester bags. The difference between the means for each type of experiment was not significant (at the 95% level). The fuse burned completely in one of the three experiments of each type.

Table IV gives the results of eight measurements on the calorimetric combustion of cyclohexylcyclohexane. The fuse burned completely in three of the eight experiments. A trace of soot was produced in one of the eight experiments. Since there was no significant carbon monoxide produced, and the result was within the range of the other experiments, it was concluded that the amount of soot produced was insignificant.

Table V gives the values for the energy of the bomb process, ΔE_c , the standard energy of combustion, ΔE_c° , and the standard enthalpy of combustion, ΔH_c° , for the three hydrocarbons. The difference between ΔE_c and ΔE_c° is the Washburn correction for the hydrocarbon. The 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 the standard benzoic acid, $\pm 0.004\%$; for the measured value of the energy equivalent of the standard calorimeter system, as given in Table I; for the combustion experiments on the hydrocarbons, as given in Tables II–IV; for the effects of impurities, 0.01% for phenylbenzene and cyclohexylcyclohexane and 0.035% for cyclohexylbenzene.

It should be noted that the form of presentation of the calorimetric data here follows the form used by 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 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 vaporization experiments were performed with the Morawetz calorimeter (15), slightly modified, using the apparatus and procedures described in a previous report (7). The samples for measurement were transported from Rice University to the University of Lund in sealed glass ampules.

Table VI gives the results of these experiments. The overall uncertainty was taken as twice the standard deviation of the mean, plus an allowance to cover possible unknown systematic errors. Within the assigned overall uncertainty, ΔH_v (298.15 K) can be taken as equal to ΔH_v° (298.15 K).

3. Previous Data

Enthalpies of combustion of all three of these compounds have been measured by earlier investigators. These previous data are presented in Table VII, along with the corresponding values from the present work. Stohmann, Kleber, and Langbein (23) (1889) and Brüll (3) (1935) reported values for 292–293 K, and their values have been appropriately corrected to standard states at 298.15 K. Estimated uncertainties have been assigned to the values of these investigators and to those of Barker (1) (1925), considering the nature of their equipment and techniques. The uncertainties of the other values are those assigned by the investigators themselves. It is seen that, except for some of the very early work, all the values are in substantial agreement within the assigned limits of uncertainty.

The only previous calorimetric measurements of enthalpies of vaporization of any of these compounds were performed on two of the compounds, in the same laboratory, with the following results: phenylbenzene (c), $81.75 \pm 0.38 \text{ kJ mol}^{-1}$, by Morawetz (16); cyclohexylcyclohexane, $58.45 \pm 0.63 \text{ kJ mol}^{-1}$, by

Table VIII. Standard Enthalpies of Formation

| Compound | | | ΔH_f° (298.15 K) | |
|------------------------------|-----------------------|----------------|-------------------------------|---|
| Molecular formula | Name | State | kJ mol^{-1} | $\text{kcal}_{\text{th}} \text{mol}^{-1}$ |
| $\text{C}_{12}\text{H}_{10}$ | Phenylbenzene | c | $+96.75 \pm 2.60$ | $+23.12 \pm 0.62$ |
| | | l ^a | $+113.40 \pm 2.65$ | $+27.10 \pm 0.63$ |
| | | g | $+178.50 \pm 2.61$ | $+42.66 \pm 0.62$ |
| $\text{C}_{12}\text{H}_{16}$ | Phenylcyclohexane | l | -79.18 ± 5.62 | -18.92 ± 1.34 |
| | | g | -19.24 ± 5.63 | -4.60 ± 1.35 |
| $\text{C}_{12}\text{H}_{22}$ | Cyclohexylcyclohexane | l | -276.35 ± 3.08 | -66.05 ± 0.74 |
| | | g | -218.37 ± 3.09 | -52.19 ± 0.74 |

^a Calculated for the hypothetical liquid at 298.15 K.

Table IX. Standard Enthalpies of Hydrogenation

| Reaction of hydrogenation | $-\Delta H^\circ$ (hydrogenation) (298.15 K), $\text{kcal}_{\text{th}} \text{mol}^{-1}$ |
|---|--|
| phenylbenzene(l) + 3H ₂ (g) = phenylcyclohexane(l) | $+46.03 \pm 1.35$ |
| phenylcyclohexane(l) + 3H ₂ (g) = cyclohexylcyclohexane(l) | $+47.12 \pm 1.39$ |
| phenylbenzene(l) + 6H ₂ (g) = cyclohexylcyclohexane(l) | $+93.15 \pm 0.73$ |
| phenylbenzene(g) + 3H ₂ (g) = phenylcyclohexane(g) | $+47.26 \pm 1.35$ |
| phenylcyclohexane(g) + 3H ₂ (g) = cyclohexylcyclohexane(g) | $+47.59 \pm 1.39$ |
| phenylbenzene(g) + 6H ₂ (g) = cyclohexylcyclohexane(g) | $+94.85 \pm 0.73$ |

Table X. Enthalpies of Complete Hydrogenation of Four Aromatic Systems

| Reaction of hydrogenation | Reference | $-\Delta H^\circ$ (hydrogenation) (298.15 K)/mol of H ₂ (g), $\text{kcal}_{\text{th}} \text{mol}^{-1}$ |
|---|--------------------------------------|---|
| Naphthalene(g) + 5H ₂ (g) = <i>trans</i> -decahydronaphthalene(g) ^a | Speros and Rossini (22) | 15.96 ± 0.14 |
| Phenylbenzene(g) + 6H ₂ (g) = cyclohexylcyclohexane(g) | This investigation | 15.81 ± 0.12 |
| Phenylcyclohexane(g) + 3H ₂ (g) = cyclohexylcyclohexane(g) | This investigation | 15.86 ± 0.46 |
| <i>n</i> -Butylbenzene(g) + 3H ₂ (g) = <i>n</i> -butylcyclohexane(g) | Prosen, Johnson, and Rossini (18) | 15.88 ± 0.17 |
| | Mean value | 15.88 ± 0.13 |

^a The value for *cis*-decahydronaphthalene would not be expected to conform.

Månsson (14). As may be noted, these earlier results are, within the assigned limits of uncertainty, in accord with the present values.

4. Standard Enthalpies of Formation and Hydrogenation

Table VIII gives the values of the standard enthalpies of formation for the three compounds, at 298.15 K, for both the liquid and gaseous states, calculated from the values of ΔH_c° and ΔH_v° from the present work, together with values of ΔH_f° for H₂O(l) and CO₂(g) from ref 4, as follows: H₂O(l), ΔH_f° (298.15 K), $-285.830 \pm 0.042 \text{ kJ mol}^{-1}$; CO₂(g), ΔH_f° (298.15 K), $-393.51 \pm 0.13 \text{ kJ mol}^{-1}$. The heat of fusion of phenylbenzene to the hypothetical liquid state at 298.15 K was taken as $3.98 \pm 0.12 \text{ kcal}_{\text{th}} \text{mol}^{-1}$, derived from work of Spaght, Thomas, and Parks (21).

Table IX gives the values of the standard enthalpies of hydrogenation for two of the compounds at 298.15 K, for both the liquid and gaseous states, calculated from the appropriate values of standard enthalpies of formation given in Table VIII. As has been stated earlier, other things being equal, the most reliable values of enthalpies of hydrogenation can be obtained from measurements of appropriate quality made by one investigator in the same laboratory with the same apparatus at the same period of time. The uncertainties for the values for hydrogenation were evaluated by omitting all uncertainties that would cancel out in the two series of experiments. Possible unknown systematic errors do not enter significantly into the uncertainties of the enthalpies of hydrogenation so calculated.

5. Discussion

Regarding the enthalpies of combustion, one can say, from

the data presented in Table VII, that all of the experimental data on these three compounds reported since 1950 are in substantial accord within the limits of uncertainty.

From the values for the enthalpies of hydrogenation presented in Table IX, one can say that, within the limits of uncertainty, the enthalpies of hydrogenation of phenylbenzene to phenylcyclohexane and of the latter to cyclohexylcyclohexane are substantially the same. This shows that, within the limits indicated, the stereochemical molecular structure is such that the two rings are essentially independent.

This leads us to consider the energy associated with the hydrogenation of aromatic rings in different molecular systems in the gaseous state. The data presented in Table X show that the enthalpy of complete hydrogenation of aromatic rings, calculated per mole of hydrogen added, has substantially the same value whether one hydrogenates naphthalene, or phenylbenzene, or phenylcyclohexane, or *n*-butylbenzene, all in the gaseous state. The mean value for the enthalpy of complete hydrogenation of these several aromatic systems is seen to be $15.88 \pm 0.13 \text{ kcal}_{\text{th}} \text{mol}^{-1}$ of H₂(g), for the gaseous state at 298.15 K.

The constancy, per mol of H₂, of the enthalpy of complete hydrogenation in the gaseous state of aromatic systems of these four different kinds will be helpful in correlating and estimating the enthalpy of hydrogenation of coal. Similar information regarding the hydrogenation of aliphatic and cyclomonolefins is given by Bartolo and Rossini (2), Rockenfeller and Rossini (19), and Labbauf and Rossini (11).

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

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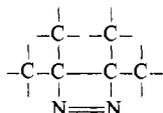
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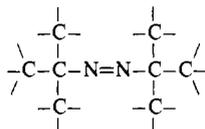
Measurements were made of the enthalpies of combustion of both compounds and of the vaporization of tetramethyldiazetene. Standard enthalpies of formation were calculated as follows, in kcal mol⁻¹: for tetramethyldiazetene, crystal +21.04 ± 0.64, gas +35.92 ± 0.69; for di-*tert*-butyldiazene, liquid -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-diazetene, 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: tetramethyldiazetene, C₆H₁₂N₂, 112.1742; di-*tert*-butyldiazene, C₈H₁₈N₂, 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*-butyldiazene 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 tetramethyldiazetene is described by Engel, Hayes, Keifer, Szilagy, and Timberlake (2). Analysis by flame ionization gas chromatography of this sample of tetramethyldiazetene 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).