

## The Enthalpies of Combustion and Formation of Diketene

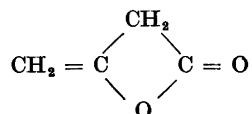
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The enthalpies of combustion and vaporization of diketene have been measured and values of the enthalpies of formation at 25.0°C have been derived. The obtained data are,  $\Delta H_f^\circ(\text{liq}) = -55.72 \pm 0.11$  and  $\Delta H_f^\circ(\text{g}) = -45.47 \pm 0.13$  kcal·mole<sup>-1</sup>, respectively. The strain energy of diketene has been estimated to be 22.5 kcal·mole<sup>-1</sup>, the same as that for  $\beta$ -propiolactone.

In connection with recent combustion work on esters (M. Månsson) it has been shown that the earlier data on esters were misinterpreted in Ref. 2. The value given for  $\Delta H_f^\circ(\text{g, hydrocarbon}) - \Delta H_f^\circ(\text{g, ester})$  should be  $71 \pm 1$  kcal·mole<sup>-1</sup>. This changes the calculated strain energy of  $\beta$ -propiolactone from 25 to 22.5 kcal·mole<sup>-1</sup>.

Diketene long remained a molecule of controversy among chemists. The question of the structure of liquid diketene was not settled until the development of nuclear magnetic resonance spectroscopy.<sup>1</sup> The structure thus confirmed is



which can be regarded as  $\beta$ -methylene- $\beta$ -propiolactone. Partly in consequence of earlier work in this laboratory it was considered of interest to find out how the introduction of a second  $sp^2$ -hybridized carbon atom in the ring would affect the strain energy of the molecule as compared to the strain in  $\beta$ -propiolactone<sup>2</sup> and its parent compound, cyclobutane. Diketene is also a very interesting compound from the point of view of polymer chemistry and this fact provided another reason for determining some of its energy relationships.

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\*\* Sponsored by the Swedish Natural Science Research Council and the Swedish Council for Applied Research.

## EXPERIMENTAL

*Material.* A commercial sample (TCI, Japan) of diketene was distilled under reduced pressure\* ( $\sim 10$  mm Hg;  $25.5-26.0^\circ\text{C}$ ) in an all-glass apparatus. The NMR-spectrum of the middle fraction indicated the presence of a few percent of some unknown impurity. The sample was further purified by fractional crystallization. About 70 % of the middle fraction from the distillation was crystallized at a slow rate, with continuous, gentle movement of the liquid and at a bath temperature of  $-8$  to  $-10^\circ\text{C}$ . The liquid was then decanted and the crystals were rinsed by melting a small fraction which was then removed by decanting. All these operations were undertaken in an all-glass, closed apparatus. The crystals were allowed to melt and the above procedure repeated (second, identical apparatus), this time freezing about 50 % of the liquid. NMR-spectra of the purified sample showed no trace of any impurity.\*\* From NMR-spectra it was also concluded that the water content of the sample should be less than 0.05 % even before the use of any drying agent. The pure diketene was stored in a polythene bottle at low temperature, and all transfers of substance were made under a stream of dry nitrogen.  $d_4^{20} = 1.0947$ ,  $d_4^{25} = 1.0887$ ;  $n_D^{20} = 1.4361$ ,  $n_D^{25} = 1.4383$ .

*Combustion calorimetry; apparatus and procedure.* The Thermochemistry Laboratory rotating-bomb calorimeter TKL-3 with bomb 3A was used.<sup>3</sup> Calibration experiments were performed according to standard procedure using the National Bureau of Standards sample 39i of benzoic acid. The paraffin oil used as auxiliary material was designated USBM-P3a.<sup>4</sup>

An earlier attempt in this laboratory to determine the heat of combustion of diketene failed, mainly due to polymerization of the substance shortly after it had been filled into soft-glass ampoules that were to be used in the combustion experiments. For this reason three soft-glass and three Pyrex ampoules were simultaneously filled with diketene. The filling tube with the ampoules, when removed from the vacuum line was closed and stored for 24 h in a refrigerator. During that time the substance in the three soft-glass ampoules turned yellow (due to polymerization), while no colouring could be seen in the Pyrex ampoules. As soon as they had reached room temperature, the latter were taken from the filling tube and sealed immediately. After storing them for about a week at room temperature without any detectable discolouring of the diketene it was considered that Pyrex ampoules would be suitable for use in the combustion experiments.

A freshly prepared, pure sample of diketene was dried over-night over regenerated Drierite,  $\text{CaSO}_4$ . The diketene was transferred to the vacuum line, dried over fresh  $\text{CaSO}_4$ , and half of the sample distilled into the receiver containing the ampoules to be filled.<sup>5</sup> All combustion experiments were carried out within three days from the filling of the ampoules. Out of ten combustions five were rejected because of small soot deposits in the glass or on the bomb walls. (Weight of ampoules 50–70 mg.)

The combustion experiments were performed under standard conditions with 0.79 ml of water in the bomb. Calorimeter data are given in Ref. 3. All weighings were reduced to mass and the molecular weight computed from the 1961 Table of atomic weights.<sup>6</sup>

*Vaporization calorimetry.* The enthalpy of vaporization at  $25.0^\circ\text{C}$  of diketene was determined using the Wadsö calorimeter.<sup>7</sup> The result is included in Table 2.

## RESULTS

The results are expressed in terms of the defined thermochemical calorie equal to 4.1840 abs.joules. All symbols used are those introduced by Hubbard, Scott and Waddington.<sup>8</sup> The  $\Delta E_\Sigma$  values were calculated using SMIL, electronic computer of the University of Lund, and therefore the calculational procedure given by Hubbard *et al.* (Ref. 8) has been slightly modified. The

\* The amount of polymer formed upon distillation is a direct function of temperature.

\*\* It was not possible to use GLC in establishing the purity of the sample.

Table 1. Results of combustion experiments on diketene.

$$\begin{aligned} \epsilon^\circ(\text{calor}) &= 6771.07 \pm 0.34 \text{ cal}\cdot\text{deg}^{-1} & M &= 84.075 \\ -\Delta E_c^\circ/M (\text{Oil}) &= 10984.4 \pm 0.9 \text{ cal}\cdot\text{g}^{-1} & P^i(\text{gas}) &= 30.0 \text{ atm} \\ -\Delta E_c^\circ/M (\text{Fuse}) &= 4017 \pm 1 \text{ cal}\cdot\text{g}^{-1} & t_h &= 25.00^\circ\text{C} \end{aligned}$$

m' g	m'' g	$\Delta t$ deg	$\Delta E_{\text{dec}}^{\text{f}}(\text{HNO}_3)$ cal	$\Delta E_\Sigma$ cal	$-\Delta E_c^\circ/M$ cal·g <sup>-1</sup>
0.651408	0.135020	0.74665	0.78	3.22	5436.02
0.667755	0.121446	0.73802	0.72	3.24	5438.21
0.612000	0.148770	0.73732	0.74	3.09	5436.72
0.641099	0.134130	0.73707	0.76	3.17	5436.43
0.650968	0.128644	0.73613	0.85	3.19	5437.36

$$-\Delta E_c^\circ/M = 5436.95 \pm 0.38^a \text{ cal}\cdot\text{g}^{-1}$$

<sup>a</sup> The uncertainty given is the standard deviation of the mean.

final over-all precision of the  $\Delta E_c^\circ$  mean value was estimated by the method of Bjellerup,<sup>9</sup> (also see Ref. 5, p. 1868). Auxiliary thermochemical data have been taken from Ref. 10.

Table 1 gives the results of the combustion experiments. The  $\Delta E_c^\circ$  value refers to the reaction in which all reactants and products are in their thermodynamic standard states at 25.0°C. Table 2 gives the standard energy,  $\Delta E_c^\circ$ , and enthalpy,  $\Delta H_c^\circ$ , of combustion for diketene together with the enthalpy of vaporization,  $\Delta H_v$ , and derived enthalpies of formation,  $\Delta H_f^\circ$ , at 25.0°C.

Table 2. Results and derived data at 25.0°C. In kcal·mole<sup>-1</sup>.

$$\begin{aligned} \Delta E_c^\circ(\text{liq}) &= \Delta H_c^\circ(\text{liq}) = -457.11 \pm 0.10^a \\ \Delta H_f^\circ(\text{liq}) &= -55.72 \pm 0.11^a \\ \Delta H_v &= 10.25 \pm 0.03^b \\ \Delta H_f^\circ(\text{g}) &= -45.47 \pm 0.13^a \end{aligned}$$

<sup>a</sup> The given uncertainty is twice the final over-all standard deviation of the mean.

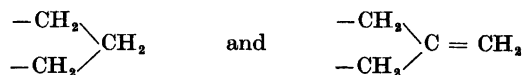
<sup>b</sup> The given uncertainty is the final over-all standard deviation of the mean.

## DISCUSSION

The heat of combustion of "dimeric ketene" at 20°C was reported in 1935 by Wassermann *et al.*<sup>11</sup> The value given for the liquid (determined by Dr. G. Becker in the laboratory of Professor W. A. Roth) was 447.1 kcal·mole<sup>-1</sup> with an estimated 456 ± 2 for the substance in the gaseous state.

Sunner *et al.*<sup>2</sup> determined the enthalpy of combustion for  $\beta$ -propiolactone and the enthalpy of formation at 25.0°C was derived:  $\Delta H_f^\circ(\text{g}) = -67.61 \pm 0.20$  kcal·mole<sup>-1</sup>. Using a group method their estimated strain energy of  $\beta$ -propiolactone is 22.5 ± 1 kcal·mole<sup>-1</sup> (*cf.* p. 171) compared to 25.5 for cyclobutane.

Their method of calculation was adopted and the  $\Delta\Delta H_f^\circ(\text{g})$  value for the difference in group enthalpies between



was calculated to be  $-22.12 \pm 0.05$  kcal·mole<sup>-1</sup> using  $\Delta H_c^\circ$  and  $\Delta H_f^\circ$  data from Ref. 12. Combined with the  $\Delta H_f^\circ(\text{g})$  value for  $\beta$ -propiolactone this gives a *calculated* enthalpy of formation for gaseous diketene of  $-45.49$  kcal·mole<sup>-1</sup>, while the value obtained in this investigation is  $-45.47 \pm 0.13$  kcal·mole<sup>-1</sup>. The identity of the two "values" implies that the strain energy of diketene equals that of  $\beta$ -propiolactone.

*Acknowledgement.* The assistance of Mrs. S. Bergström in performing some of the enthalpy of vaporization experiments is gratefully acknowledged. This investigation was supported by a special grant from the *Swedish Council for Applied Research*.

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Received July 28, 1967.