

## Heats of Combustion of Cyclic Ketones and Alcohols

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Values are reported for the heats of combustion of *cyclopentanone*  $-686.91 \pm 0.22$  kcal/mole; *cyclopentanol*  $-740.47 \pm 0.20$ ; *cyclohexanone*  $-841.04 \pm 0.25$ ; *cyclohexanol*  $-890.99 \pm 0.26$ .

Heats of hydrogenation of the cyclic ketones derived from these data are in reasonable agreement with those from direct measurements, and are used in a discussion of the steric strain energies of the five- and six-membered rings.

The heat of hydrogenation of *cyclohexanone* ( $-15.4$  kcal) determined by Kistiakowsky *et al.*<sup>1</sup> is apparently anomalous since it would be expected to lie near the figures for straight chain ketones, *e.g.* acetone ( $-13.41$ ) and methyl ethyl ketone ( $-13.19$ )<sup>2</sup>, if the ring is assumed to be strain free. The value for *cyclopentanone* ( $-12.5$ ) has also been under discussion, and it was therefore decided to determine the heats of hydrogenation of the cyclic ketones *via* their heats of combustion and the heats of combustion of the corresponding alcohols.

The only existing literature value for the ketones is that of Roth<sup>3</sup> for *cyclopentanone*. The heats of combustion of *cyclopentanol* and *cyclohexanol* have been determined by Parks and co-workers<sup>4</sup>. *Cyclohexanol* has also been studied much earlier by Richards and Davis<sup>5</sup>.

### MATERIALS

*Cyclopentanone* of purum grade was distilled twice at reduced pressure through a 10-plate column and the main-fraction was distilled through a 32-plate column, the fraction boiling between  $130.2 - 130.6^\circ\text{C}$  at 757 mm Hg being kept for further treatment. Most of the water in the sample was removed azeotropically at  $94^\circ\text{C}$  but gas-liquid chromatography (LAC-3R-726 as liquid phase) showed that some water was still present, although all organic impurities had been removed. The sample was then shaken with anhydrous potassium carbonate, filtered, and infra red spectra taken of the pure sample and of the sample with known added amounts of water. From the spectra the water content of the sample was calculated to be between 0.02 and 0.03 %.

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*Cyclopentanone*. This substance was prepared by hydrogenation of *cyclopentanone* using the method of Noller and Adams <sup>6</sup>, with Adams platinum oxide as catalyst. Similar treatment and analysis to above gave a sample free from organic impurities and water.

*Cyclohexanone*. A purum grade sample was repeatedly distilled at different pressures. Five distillations were required before all the *cyclohexanol* was removed. The sample was dried by treating with  $P_2O_5$  and distilling. Infra red spectra and melting curves \* showed the absence of all impurities.

*Cyclohexanol*. The purum grade sample was found to be very hygroscopic and contained a considerable amount of water even after several fractional distillations. By repeated slow freezing and evaporation under vacuum most of the water was removed but it proved impossible to remove all of it. By the use of accurate infra red spectrometry a calibration curve was obtained for water content of the sample, by taking spectra of the pure sample and the sample with known amounts of added water. The water content was found to be  $0.10 \pm 0.02$  %.

Table 1 gives the physical constants of the compounds and amounts of impurities.

Table 1. Physical constants.

Substance	Bp 760 mm corr. °C	m.p. °C **	$d_4^{25}$	$n_D^{25}$	% water
<i>Cyclopentanone</i>	130.7	-53.1	0.94368	1.4352	0.03
<i>Cyclopentanol</i>	140.8	-***	0.94229	1.4515	0.00
<i>Cyclohexanone</i>	155.6	-32.1	0.94010	1.4497	0.00
<i>Cyclohexanol</i>	161.2	23.91	0.94506	1.4641	0.10

#### COMBUSTION CALORIMETRY

The calorimetric system used was that described by Bjellerup <sup>7</sup>, with the exception that the rotating mechanism was not used. Since all the compounds were contained in glass ampoules, a platinum baffle and shield were placed over the crucible to avoid splashing of the sample when the ampoule burst on ignition <sup>8</sup>. As an auxiliary fuel to aid combustion paraffin oil of known heat of combustion <sup>9</sup> was used. After each combustion, the amount of nitric acid present was determined by potentiometric titration against standard alkali.

In each combustion experiment the calorimeter can was filled with water until a fixed total weight of calorimeter with mounted bomb was reached. This required the amount of water in the calorimeter to vary with the mass of contents in the bomb, and the energy equivalent of the system consists of:  $\epsilon^\circ$  (Calor), the energy equivalent of a standard system consisting of the whole system assembled as normally but with no contents in the bomb *i.e.* no removable matter;  $C_p(H_2O)m^1$  (Cont.), the energy equivalent of an amount of water equal in mass to the bomb contents;  $\epsilon^i$  (Cont.), the energy equivalent of the contents of the bomb.

*Calibration*. The calorimetric system was calibrated by the combustion of benzoic acid (NBS sample 39 h), under conditions specified in the accompanying certificate <sup>10</sup>. The results of the calibration experiments are given in Table 2.

\* Melting curves were obtained by the use of a glass enclosed platinum resistance thermometer of dimensions 20 by 4 mm, surrounded by a thin layer of sample.

\*\* from melting curves. \*\*\* no defined m.p. due to formation of glass.

Table 2. Results of calibration experiments.

$t_h = 25.0^\circ\text{C}$	$V(\text{Bomb}) = 0.2751 \text{ litre}$	$m(\text{Cont.}) = 36.26 \text{ g}^*$		
$t_i = 24.1^\circ\text{C}$	$V(\text{H}_2\text{O tot.}) = 0.820 \text{ ml}$	$-\Delta E_c/M (\text{Benzoic Acid}) = 6\,317.87$		
$P(\text{gas}) = 30.0 \text{ atm}$	$m(\text{Pt}) = 23.690 \text{ g}$	$-\Delta E_c/M (\text{Fuse}) = 3\,971 \pm 4 \text{ cal/g}$		
		$\pm 0.62 \text{ cal/g}$		
		$e(\text{Cont.}) = 3.96 \text{ cal/deg}^*$		

$m'$	$m'''$	$\Delta t$	$-\Delta E(\text{HNO}_3)$	$-\Delta E_{\text{I.B.P.}}/\Delta t$
g	g	deg	cal	cal/deg
0.826338	0.004721	0.88827	2.22	5900.95
0.826406	0.004973	0.88864	2.44	5900.36
0.824306	0.004947	0.88647	2.39	5899.66
0.824446	0.005188	0.88652	1.66	5900.58
0.826637	0.004963	0.88942	2.09	5896.42
0.825514	0.004894	0.88736	2.05	5901.75
				Mean = 5899.91
				Standard deviation of mean $\pm 0.76$
				$e^\circ (\text{Calor}) = 5932.21 \pm 0.76 \text{ cal/deg}$

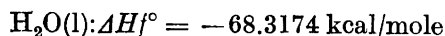
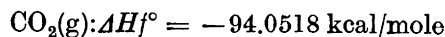
\* These values are the same for all experiments, so the mean is taken before they are included.

## RESULTS

The results of the combustions on the compounds under investigation are given in Tables 3–6. The symbols used are those of Hubbard, Scott, and Waddington<sup>11</sup>. All calorimetric quantities are expressed in terms of the defined calorie, which is equal to 4.1840 absolute joules, and all weighings are reduced to mass. The molecular weight for each compound is based upon the 1954 International Atomic Weights. The uncertainties given are the final overall standard deviations. Washburn corrections were applied as described by Hubbard, Scott, and Waddington<sup>11</sup>. The values have been corrected where necessary for the water contents of the samples.  $\Delta H_c^\circ$  values were computed using the relation

$$\Delta H_c^\circ = \Delta E_c^\circ + \Delta nRT$$

where  $\Delta n$  is the change in the number of moles of gas accompanying the combustion reaction. Heats of formation were calculated using the heat of formation values at  $25^\circ\text{C}$ <sup>12</sup>.



## HEATS OF VAPORISATION

The heats of vaporisation of the four compounds were determined calorimetrically\*\* in an apparatus which has been previously described<sup>13</sup>.

\*\* The co-operation of Dr. and Mrs. Ingemar Wadsö of this laboratory is gratefully acknowledged.

Table 3. Cyclopentanone.

$t_h = 25.0^\circ\text{C}$	$V(\text{Bomb}) = 0.2751 \text{ litre}$	$\epsilon^\circ (\text{Calor}) = 5932.21 \pm 0.76 \text{ cal/deg}$
$t_i = 24.1^\circ\text{C}$	$V_i(\text{H}_2\text{O tot.}) = 0.820 \text{ ml}$	$-\Delta E_c^\circ/M (\text{Oil}) = 10\,986.6 \pm 0.6 \text{ cal/g}$
$P_i (\text{gas}) = 30.0 \text{ atm}$	$m(\text{Pt}) = 23.69 \text{ g}$	$-\Delta E_c^\circ/M (\text{Fuse}) = 3\,971 \pm 4 \text{ cal/g}$
	$M = 84.11$	$\epsilon^i (\text{Cont.}) = 3.84 \text{ cal/deg}$
		$m^i (\text{Cont.}) = 36.14 \text{ g } \Delta E_\Sigma = 2.09 \text{ cal}$

$m'$ g	$m''$ g	$m'''$ g	$\Delta t$ deg	$-\Delta E(\text{HNO}_3)$ cal	$-\Delta E_c^\circ/M$ cal/g
0.422345	0.159776	0.004243	0.88511	1.82	8158.99
0.445034	0.149969	0.004324	0.89710	1.91	8143.15
0.432500	0.137313	0.004261	0.85694	3.08	8150.68
0.454633	0.132005	0.004414	0.87787	2.99	8152.71
0.370645	0.192849	0.004303	0.87521	2.55	8156.48
0.452351	0.133419	0.004842	0.87879	2.46	8159.81
					Mean 8153.63
					Standard deviation of mean $\pm 2.7$
					$-\Delta E_c^\circ = 685.83 \pm 0.22 \text{ kcal/mole}$

## DISCUSSION

In Tables 7 and 8 the results of the present work are summarized, together with data from the literature. It can be seen that the heats of combustion obtained here lead to heats of hydrogenation of the cyclic ketones which are about 1 kcal/mole lower than those of Kistiakowsky *et al.*

The heats of combustion of the alcohols are in excellent agreement with those obtained by Parks and co-workers.

The heats of hydrogenation of the cyclic ketones may be used in a discussion of the strain energies of these compounds and of their hydrogenation products, the alcohols.

Table 4. Cyclopentanol.

$t_h = 25.0^\circ\text{C}$	$V(\text{Bomb}) = 0.2751 \text{ litre}$	$\epsilon^\circ (\text{Calor}) = 5932.21 \pm 0.76 \text{ cal/deg}$
$t_i = 24.1^\circ\text{C}$	$V_i(\text{H}_2\text{O tot.}) = 0.820 \text{ ml}$	$-\Delta E_c^\circ/M (\text{Oil}) = 10\,986.6 \pm 0.6 \text{ cal/g}$
$P_i (\text{gas}) = 30.0 \text{ atm}$	$m(\text{Pt}) = 23.690 \text{ g}$	$-\Delta E_c^\circ/M (\text{Fuse}) = 3971 \pm 4 \text{ cal/g}$
	$M = 86.13$	$\epsilon^i (\text{Cont.}) = 3.63 \text{ cal/deg}$
		$m^i (\text{Cont.}) = 36.12 \text{ g } \Delta E_\Sigma = 1.78 \text{ cal}$

$m'$ g	$m''$ g	$m'''$ g	$\Delta t$ deg	$-\Delta E(\text{HNO}_3)$ cal	$-\Delta E_c^\circ/M$ cal/g
0.450705	0.116581	0.004168	0.87614	2.95	8579.71
0.458209	0.119113	0.003989	0.89096	2.82	8571.11
0.451100	0.118264	0.004256	0.88011	2.82	8582.66
0.407453	0.147699	0.003999	0.87104	2.52	8580.20
0.433886	0.135402	0.004271	0.88641	3.66	8574.85
0.468391	0.123072	0.004185	0.91426	2.54	8584.37
					Mean: 8578.22
					Standard deviation of mean $\pm 2.4$
					$-\Delta E_c^\circ = 739.15 \pm 0.20 \text{ kcal/mole}$

Table 5. Cyclohexanone.

$t_h = 25.0^\circ\text{C}$	$V(\text{Bomb}) = 0.2751 \text{ litre}$	$\epsilon^\circ (\text{Calor}) = 5930.29 \pm 0.76 \text{ cal/deg}^*$
$t_i = 24.1^\circ\text{C}$	$V^i(\text{H}_2\text{O tot.}) = 0.820 \text{ ml}$	$-\Delta E_c^\circ/M (\text{Oil}) = 10\,986.6 \pm 0.6 \text{ cal/g}$
$P^i (\text{gas}) = 30.0 \text{ atm}$	$m(\text{Pt}) = 23.692 \text{ g}$	$-\Delta E_c^\circ/M (\text{Fuse}) = 3971 \pm 4 \text{ cal/g}$
	$M = 98.14$	$\epsilon^i (\text{Cont.}) = 3.81 \text{ cal/deg}$
		$m^i (\text{Cont.}) = 36.26 \text{ g } \Delta E_\Sigma = 2.00 \text{ cal.}$

$m'$ g	$m''$ g	$m'''$ g	$\Delta t$ deg	$-\Delta E (\text{HNO}_3)$ cal	$-\Delta E_c^\circ/M$ cal/g
0.449731	0.121876	0.004465	0.88308	2.29	8555.18
0.445930	0.125748	0.004651	0.88532	2.62	8558.74
0.445556	0.128251	0.004505	0.88929	2.24	8560.11
0.444189	0.127791	0.004313	0.88566	2.37	8551.16
0.380247	0.178054	0.004769	0.88727	2.88	8554.96
0.571384	0.097524	0.004268	1.01494	2.95	8563.29
0.571871	0.069726	0.004523	0.96349	1.77	8559.79

Mean: 8557.46

Standard deviation of mean  $\pm 2.6$  $-\Delta E_c^\circ = 839.84 \pm 0.25 \text{ kcal/mole}$ 

\* Calculated from previous value after a small mechanical change in the bomb.

Cyclopentanone is known to be a puckered non-planar ring<sup>14</sup> and Pitzer<sup>15</sup> has calculated its torsional strain energy to be about 2.8 kcal/mole less than that of cyclopentane. The ketone, however, will have a greater C-C-C bond angular strain due to the double bond of the carbonyl group, and the value for methylene-cyclopentane (0.9 kcal/mole)<sup>15</sup> may be taken. Thus cyclopentanone has about 1.9 kcal/mole less strain energy than cyclopentane.

Since the heat of hydrogenation of cyclopentanone is less than those of straight chain ketones, steric effects in the product *i.e.* cyclopentanol, must be

Table 6. Cyclohexanol.

$t_h = 25.0^\circ\text{C}$	$V(\text{Bomb}) = 0.2751 \text{ litre}$	$\epsilon^\circ (\text{Calor}) = 5959.23 \pm 0.74 \text{ cal/deg}^*$
$t_i = 24.1^\circ\text{C}$	$V^i(\text{H}_2\text{O tot.}) = 0.820 \text{ ml}$	$-\Delta E_c^\circ/M (\text{Oil}) = 10\,986.6 \pm 0.6 \text{ cal/g}$
$P^i (\text{gas}) = 30.0 \text{ atm}$	$m(\text{Pt}) = 23.696 \text{ g}$	$-\Delta E_c^\circ/M (\text{Fuse}) = 3971 \pm 4 \text{ cal/g}$
	$M = 100.14$	$\epsilon^i (\text{Cont.}) = 3.71 \text{ cal/deg}$
		$m^i (\text{Cont.}) = 36.32 \text{ g } \Delta E_\Sigma = 1.92 \text{ cal}$

$m'$ g	$m''$ g	$m'''$ g	$\Delta t$ deg	$-\Delta E(\text{HNO}_3)$ cal	$-\Delta E_c^\circ/M$ cal/g
0.444036	0.116563	0.004623	0.88472	2.23	8873.80
0.433960	0.122207	0.004490	0.88016	2.01	8876.39
0.437664	0.118886	0.004691	0.87904	1.76	8868.21
0.456876	0.110529	0.004530	0.89642	2.38	8877.99
0.442470	0.119468	0.004722	0.88618	2.11	8874.60
0.441523	0.120471	0.004586	0.88001	2.61	8870.71

Mean: 8873.61

Standard deviation of mean  $\pm 2.6$  $-\Delta E_c^\circ = 888.78 \pm 0.26 \text{ kcal/mole}$ 

\* Measured after gasket of bomb had been changed.

Table 7. Heats of combustion, vaporisation and formation at 25° C

Substance	$-\Delta H_c^\circ(l)$	$-\Delta H_f^\circ(l)$	$\Delta H_v$	$-\Delta H_f^\circ(g)$	Earlier work $-\Delta H_c^\circ(l)$
Cyclopentanone	686.91 $\pm$ 0.22	56.52	10.21	46.31	683.8 <sup>3</sup>
Cyclopentanol	740.47 $\pm$ 0.20	71.37	13.74	57.63	740.07 <sup>4</sup>
Cyclohexanone	841.04 $\pm$ 0.25	64.86	10.77	54.09	—
Cyclohexanol	890.99 $\pm$ 0.26	83.23	14.82	68.41	890.77 <sup>4</sup> 890.0 <sup>5</sup>

Table 8. Heats of hydrogenation.

Substance	This work	Kistiakowsky <i>et al.</i>
Cyclopentanone	-11.32	-12.26 <sup>a</sup>
Cyclohexanone	-14.32	-15.23 <sup>a</sup>
Acetone		-13.29 <sup>a</sup>
Methyl ethyl ketone		-13.07 <sup>a</sup>

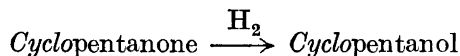
<sup>a</sup> Corrected from 82°C to 25°C.

Table 9. Heats of formation of cycloparaffins and alcohols.

n	$C_nH_{2n}$	$C_nH_{2n-1}OH$	$\Delta(H \rightarrow OH)$
5	-18.46	-57.63	-39.17
6	-29.43	-68.41	-38.98

greater than those in the reactant. In other words, part of the energy occurring during the hydrogenation process is retained by the product molecule as steric energy.

By considering the heats of formation of the five- and six-membered cycloparaffins<sup>16</sup> and their alcohols, and assuming the six-membered rings to be free from strain (at 25°C), the strain energy of cyclopentanol is seen to be virtually the same as that in cyclopentane (Table 9). Thus, the process



results in an increase in strain energy of approximately 1.9 kcal and we would expect the heat of hydrogenation to be less by this amount than those of the straight chain ketones (-13.3).

The experimental figure is almost exactly 1.9 kcal but such good agreement is fortuitous since there is an uncertainty of a few tenths of a kilocalorie. The above discussion on the strain energies of the five-membered rings would, however, seem to be valid.

Disagreement has existed on the question of strain in the cyclohexanone molecule. Brown *et al.*<sup>17</sup> have proposed that strain does exist, the structural explanation being strain associated with the opposed orientation of the double bond relative to the C—H bonds of adjacent ring methylene groups. Allinger<sup>18</sup> has supported this view and gave a value of 1.6 kcal for the strain energy of

*cyclohexanone*. Pitzer<sup>15</sup> on the other hand has been inclined to the view that the molecule is unstrained, as shown by microwave studies<sup>19</sup> which have the opposed orientation as the stable one.

The thermochemical data given here show that *cyclohexanone* has a heat of hydrogenation about 1 kcal greater than those of straight chain ketones, and on this basis it will have a strain energy of about 1 kcal if its hydrogenation product, *cyclohexanol*, is assumed to be free from strain.

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