The Heat of Combustion and Polymerization of

β-Propiolactone

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From combustion and vaporization experiments on β-propiolactone the following derived heat of formation data at 25.0° were obtained: $\Delta Hf°$(liq) = −78.85 ± 0.20 and $\Delta Hf°$(g) = −67.61 ± 0.20 kcal.-mole⁻¹, respectively. By comparison with the alkyl alkanoates the strain energy of the lactone was estimated to be ca. 25 kcal.mole⁻¹. The heat of propagation of the polymerization of propiolactone was determined at 25°: ΔH = −19.2 ± 0.9 kcal per mole of monomer unit.

β-Propiolactone (PL) is an interesting compound both from a theoretical as well as from a practical point of view. It is a four-membered oxygen heterocyclic with a sp^2-hybridized ring carbon. The question arises whether the strain energy of this compound is larger or smaller than that of the parent ring compound, cyclobutane. Also, PL is of potential interest as a monomer — by γ-irradiation in the crystalline state a very high molecular weight polyester may be obtained.[1] For the polymerization process it is of some importance to know if the strain energy of the PL-molecule is completely released upon polymerization or not.

EXPERIMENTAL

Materials. A commercial sample of PL was distilled twice under vacuum through a 50 cm all-glass column filled with helices. B.p. 49.5° at 11 mm Hg (uncorr.). The substance polymerized easily and for this reason GLC could not be used. In several attempts with different stationary phases the sample quantitatively remained on the filling and not even traces of substances passing the column could be detected.

The water content of the same sample as was used for the combustion experiments was determined by a method developed in this laboratory.[2] It was found to be less than 0.005 wt %.

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Combustion calorimetry, apparatus and procedure. The Thermochemistry Laboratory rotating-bomb calorimeter was used.[3] Calibration experiments were performed according to standard procedure using National Bureau of Standard sample 39i of benzoic acid. The paraffin oil used was designated USBM-P3a (*cf.* Ref. 4).

The sample of PL was transferred to a vacuum line, dried over CaH_2, and distilled into a receiver, from which the ampoules for combustion experiments and for the determination of water content and physical constants were filled.[5] The combustions were performed under standard conditions using 0.8 ml of water in the bomb. All weighings were reduced to mass and the molecular weights were computed from the 1961 table of atomic weights.[6]

Heat quantities are given in thermochemical calories, defined by 1 cal = 4.184 abs. joules and refer to the isothermal process at 25°. The results were calculated using SMIL, electronic computer of the University of Lund. For this purpose the calculational procedure given by Hubbard *et al.*[7] was slightly modified.

Polymerization calorimetry, apparatus and procedure. A Calvet heat flow calorimeter manufactured by DAM, Lyon, France, was used.[8] The high sensitivity galvanometer and Sefram galvanometer spot follower allowed the recording of the signal from the 992 junctions 40 Ω thermopile. The sensitivity was reduced to 1/40 by short circuiting the pile with a 1 Ω resistance. A thermal junction was inserted in the aluminium block to enable the precise recording of the temperature of the calorimeter.

The polymerization was carried out at 25° using KOH as an ionic catalyst. In order to achieve a smooth, quantitatively well-defined reaction, the standard stainless-steel cell calorimeters were modified (Fig. 1). Dried KOH (1 to 6 mg) was kept in the upper
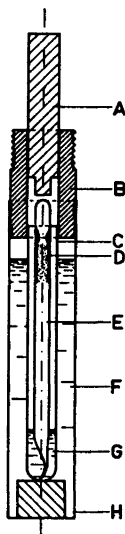

Fig. 1.

part of an evacuated, sealed capillary tube (E), the lower end of which had been drawn out to a fine capillary with a bend. The total volume of the tube was approx. 0.3 ml. The tip rested against the bottom of a glass tube (C) which contained an excess of PL (G). The outer glass tube was centered inside the steel cell (H) containing silicon oil (F) as heat transfer medium. The cell was closed by a teflon stopper (B) through which was carried a snugly fitting rod of plexiglass (A) resting on the sealed ampoule. By giving the plexiglass rod a slight push using a glass tube going all the way from the cell to the outside of the calorimeter, the tip of the sealed tube was broken, the PL samples sucked in, and the reaction started.

Tris(hydroxymethyl)aminomethane (tris) was used to calibrate the calorimeter.[9] In this case the stainless-steel cell was charged with 10 ml 0.1 N hydrochloric acid, and the tris sample (35—70 mg) was contained in a small cylindrical glass ampoule with a very thin bottom. The lack of stirring in the Calvet calorimeter is a serious draw-back which necessitated the use of a special technique for achieving the dissolution of the tris in the acid. If loose tris crystals were used, they fell down to the bottom of the cell and equilibrium was not reached within a reasonable length of time. Therefore, the tris sample was carefully melted inside the glass ampoule in such a way that on cooling it crystallized to a thin film adhering *only* to the cylindrical wall. When the bottom of the ampoule was broken, acid entered the cell and the tris sample was dissolved within less than 10 min. The equalling out of the concentration gradient took a rather long time. However, the accompanying heat effect was found to be insignificant in relation to the precision of the measurements.

The polymerization reaction and its stoichiometry. The polymerization was confined to the interior of the capillary tube. The state of the KOH affected very much both the rate of the reaction and its yield. The KOH was prepared by dissolving analytical grade pellets (12.2 % water) in MeOH to obtain a saturated solution. A small amount of this solution was introduced at the bottom of the capillary tube. Excess methanol and water were removed by drying at room temperature in vacuum for 4 and 9 h. The capillary tube was then sealed under vacuum. The solid deposit consisted of 62 % KOH (4 h of drying) and 81 % KOH (9 h) in water and methanol.

KOH prepared in this way dissolved fast in PL and a precipitation of polymer was observed after about 30 min. The total duration of the reaction was from 24 to 36 h. The yield of polymer, calculated on the amount of PL inside the capillary tube, varied from 70 to 97 %. It was determined by carefully washing the polymer with methanol and drying in vacuum to constant weight.

The m.p. of the polymer was found to be 107—109° which indicates a satisfactory molecular weight (m.p. 94—97° corresponds to *ca.* 100 monomer units [10]).

Vaporization calorimetry. The heat of vaporization of PL was determined using the Wadsö calorimeter.[11]

Table 1. Heat of combustion of PL.

$\varepsilon°(\text{Calor}) = 6796.46 \pm 0.63$ cal·deg^{-1}; $-\Delta E_c°/M(\text{Oil}) = 10984.4 \pm 0.9$ cal·g^{-1};
$-\Delta E_c°/M(\text{Fuse}) = 3971 \pm 4$ cal·g^{-1}

$M = 72.064$		$P^i(\text{gas}) = 30.0$ atm.			$t_h = 25.00°$
m' g	m'' g	Δt deg	$\Delta E^f_{dec.}(\text{HNO}_3)$ cal	ΔE_{Σ} cal	$-\Delta E_c°/M$ cal·g^{-1}
0.622364	0.173466	0.71865	2.41	2.95	4714.48
0.623450	0.176719	0.72556	1.80	2.98	4722.37
0.625389	0.183875	0.73718	1.70	3.02	4713.29
0.715286	0.144776	0.73749	1.67	3.24	4718.44
0.700135	0.151778	0.73809	0.78	3.20	4720.25
0.673846	0.161040	0.73502	1.78	3.10	4715.61
0.703923	0.150035	0.73734	3.33	3.21	4715.48

$-\Delta E_c°/M = 4717.1 \pm 1.3$

$\Delta E_c°(\text{liq}) = \Delta H_c°(\text{liq}) = -339.93 \pm 0.20$ * kcal.mole^{-1}
$\Delta H f°(\text{liq}) = -78.85 \pm 0.20$ kcal.mole^{-1} **
$\Delta H_{vap}° = 11.24 \pm 0.01$ kcal.mole^{-1}
$\Delta H f°(\text{g}) = -67.61 \pm 0.20$ kcal.mole^{-1}

* The given uncertainty is twice the final over-all standard deviation of the mean.
** Linnell and Noyes [13] determined this datum to -71 ± 7 kcal. mole^{-1}.

RESULTS

Heat of combustion experiments. The results of the combustion experiments are given in Table 1. For explanation of symbols see Ref. 7. Calorimeter data are given in Ref. 3.

Heat of polymerization experiments. Seven calibration runs with tris were performed. The value for the heat of solution of 5 mmoles of tris in 10 ml of 0.1 M HCl was taken as $\Delta H = -7.112$ cal.mole^{-1} (Ref. 12). The amount of tris in the runs varied between 0.3 and 0.6 mmole — within these limits the deviation from the value chosen is insignificant.

The calibration constant of the calorimeter was found to be 0.252 ± 0.005 cal per cm^2 area under the recorded temperature-time curve. Blank tests showed the absence of heat effects caused by the manipulation which had to be done when the reaction was started.

A series of seven polymerization experiments was performed, the results of which are presented in Table 2.

Table 2. Polymerization of PL.

| Amount in mg of | | Yield | Area | $-\Delta H$ |
KOH *	polymer	%	cm^3	kcal.mole^{-1}
3.75	287.4	90	293.6	18.5
3.13	116.1	80	132.5	20.7
5.43	293.2	92	316.9	19.6
3.78	319.5	89	357.3	20.3
1.43	135.7	70	138.2	18.5
6.44	354.6	91	372.1	19.1
2.92	377.9	97	391.9	18.8
				Ave. 19.4 ± 0.3**

* Net amounts. The KOH was dried for 4 and 9 h in the 5 first and 2 last experiments, respectively.
** Twice the over-all standard deviation ± 0.9.

DISCUSSION

The strain energy in PL. In order to calculate the strain energy of PL, a comparison is made between enthalpies of n-alkyl alkanoates and n-alkanes: RCOOR' and RCH$_2$CH$_2$R'. This procedure is equivalent to a group method; the obtained average $\Delta\Delta H$ value represents the difference between group enthalpies for $-CH_2CH_2-$ and $-CO \cdot O-$. Practically all values of enthalpies of formation of esters go back to Schjånberg's work.[14], * These determinations, however, are impared by systematic errors, some of which cannot be corrected

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* Recently, highly accurate values were published for a number of methyl alkanoates.[15] The methyl esters, however, differ by as much as 5 kcal from the additivity scheme and were therefore not considered here.
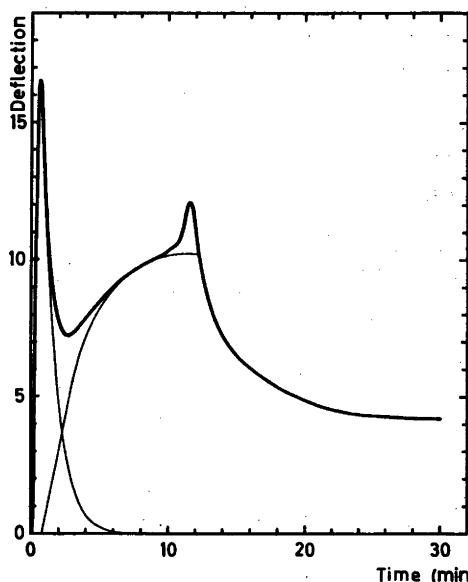
Fig. 2.

for afterwards. Probably, the most important error is that heat of combustion values of low-boiling compounds are too low, an error which decreases with increasing b.p. of the compounds. Therefore we have chosen for comparison the five esters propyl and butyl propionate, ethyl, propyl and butyl butyrate. Schjånberg's data have been recalculated to 25° and his estimates of enthalpies of vaporization have been replaced using Klages formula with constants calculated by Wadsö.[16] The average result for $\Delta \Delta Hf°(g) = \Delta Hf°(g, \text{hydro-carbon}) - \Delta Hf°(g, \text{ester}) = 73.5 \pm 1$ kcal.mole^{-1}.

If we now compare enthalpy of formation data of PL and cyclobutane [17] and take into account the strain energy of the last compound, 25.5 kcal.mole^{-1} (Ref. 18), we get the strain energy of PL to 25 ± 1 kcal.mole^{-1}. Non-bonded interactions should be smaller in PL than in cyclobutane whereas the sp^2 carboxyl carbon should lead to an increased strain in the ring. From the result it might seem that these effects of opposite sign cancel out.

The heat of polymerization. A representative heat of polymerization curve is shown in Fig. 2. Two characteristic peaks are seen; one occurs within 1 min after the start of the reaction, the second after 10 to 12 min. The initial peak must be due to the dissolution of KOH possibly in connection with a primary reaction step which then must be very fast — the peak width is only *ca.* 3 min. The area under the peak can be estimated if it is assumed that the fall-off branch of the peak is exponential and follows the same equation as is valid for an instantaneous reaction taking place in the calorimeter:

$$y = y_0 \times e^{-k}$$

where y is the deflection at time t (in min). For our system $k = 1.0$. By choosing a suitable value for y_0 the difference between the recorded curve and the

given function in the approximate interval $1 \leq t \leq 6$ becomes a smooth curve, which then should represent the heat evolved during the propagation of the polymerization.

It was found that the amount of heat evolved during the initial reaction was proportional to the amount of KOH present, and roughly equal to 50 kcal per mole of KOH. From the magnitude of the heat effect it is evident that *one* ring opening must be involved in the initial reaction. The heat of solution of KOH in PL can only be guessed at but it should be at least 6 and not exceed 10 kcal.mole^{-1}. The ring opening by KOH must include some kind of a neutralization reaction — the initial reaction product might be written $K^+O^-COCH_2CH_2OH$. The heat of neutralization should be approximately 12—14 kcal.mole^{-1} and the release of strain energy amounts to *ca.* 25 kcal. Summing up, one obtains a total heat release accompanying the initial processes of 43—49 kcal.

The result is not surprising — the first reaction step in which the cyclic ester is hydrolyzed by very concentrated KOH under simultaneous release of a large amount of strain energy should be very fast compared to the propagation steps in which the less reactive potassium carboxylate is involved.
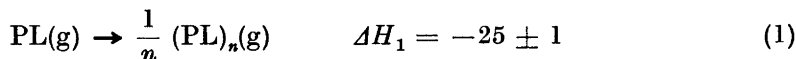
The general shape of the curve after the initial reaction indicates an increasing rate of polymerization ending in a small peak 10 to 12 min after the start of the reaction. In the absence of experimental data on the system other than heat properties, an explanation for the thermal behaviour cannot be given, though it seems likely that it is connected with changes in viscosity during the polymerization. It should be noted that the maximum deflection is reached when the reaction is about 1/3 completed. The area under the small peak corresponds to less than 1 % of the total amount of heat given off and the possibility cannot be excluded that the peak is caused by an artefact.

The heat of polymerization values given in Table 2 are based on the total amount of heat given off and the total weight of polymer. The heat of propagation of the polymerization reaction counted per monomer unit can be obtained by subtracting the amount of heat corresponding to the first peak and the weight of the KOH plus an equimolar amount of PL. The heat of propagation then becomes (A and B are end groups):
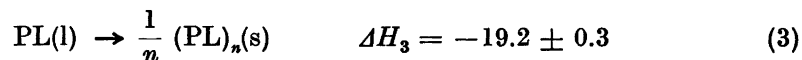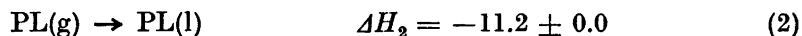
$$A(PL)B(liq) + n(PL)(liq) \rightarrow A(PL)_{n+1}B(s)$$
$$-\varDelta H = (19.2 \pm 0.3) \times n \text{ kcal.}$$
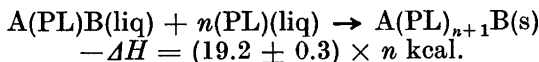
It is sometimes stated that the heat of polymerization of a small-ring compound should equal the thermochemical strain energy of the monomer.[19]

An implicit assumption must then be that the long chain polymer in the gaseous state should be energetically comparable to the reference model used in calculating the strain energy of the monomer. An experimental verification seems to be impossible to achieve as the high molecular weight of a polymer prevents very effectively measurements of heat of vaporization. However, an indirect illustration of the validity of the statement can be given. If we assume that it is true, the following equation is valid ($\varDelta H$ in kcal):

$$PL(g) \rightarrow \frac{1}{n}(PL)_n(g) \qquad \varDelta H_1 = -25 \pm 1 \qquad (1)$$

Besides,

$$PL(g) \rightarrow PL(l) \qquad \Delta H_2 = -11.2 \pm 0.0 \qquad (2)$$

$$PL(l) \rightarrow \frac{1}{n}(PL)_n(s) \qquad \Delta H_3 = -19.2 \pm 0.3 \qquad (3)$$

Finally for the heat of sublimation of the polymer

$$\frac{1}{n}(PL)_n(s) \rightarrow \frac{1}{n}(PL)(g) \quad \Delta H_4 \qquad (4)$$
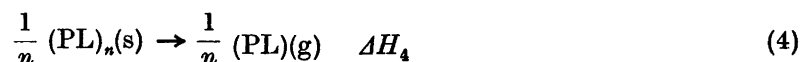
Now, $(1)-(2)-(3) = (4)$ and $\Delta H_4 = 5.4 \pm 1.1$

Thus the assumption leads to the result that the heat of sublimation of the PL polymer should be between 4.3 and 6.5 kcal per mole of monomer unit. In a recent paper, Davies and Hybett [20] studied the sublimation heats of long-chain methyl esters. They found the lattice energy increments for a $-CO-O-$ and a CH_2-group to be 4.6 and 1.95 kcal, respectively. Thus, for a long-chain polyester with $-CH_2-CH_2-CO-O-$ units, one would expect a heat of sublimation of roughly 8.5 kcal per unit.

The discrepancy between the two heat of sublimation values can be attributed to one or several of the following causes. A perfect polymer crystal lattice can be 'strained' compared to the reference used — long-chain methyl alkanoates. The samples of the polymer obtained in this work may exhibit lattice defects causing strain. Finally, the assumption made in the beginning can be wrong.

The heat of fusion of a truly crystalline PL polymer should not exceed ca. 3.2 kcal per mole of monomer unit, corresponding to 45 cal per g. By use of a Perkin Elmer differential scanning calorimeter the heat of fusion of an actual sample of polymer obtained in this work was found to be 1.8 kcal. per mole of monomer unit. Any strain energy in our sample should therefore not exceed 1.5 kcal. Taking into account the uncertainties in figures given, the gap between the heat of sublimation values could well be accounted for without changing the first very simple assumption that the heat of polymerization (to a gaseous polymer) equals the thermochemical strain energy.

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