

The Polymerization of 1,3-Dioxepan I—Structure of Polymer and Thermo- dynamics of its Formation, and a Note on 1,3-Dioxan

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1,3-Dioxepan was polymerized under vacuum in methylene dichloride solution by anhydrous perchloric acid. The reaction involves a perfectly clean monomer-polymer equilibrium. The oligomers and polymers are cyclic and are formed by a ring-expansion mechanism. For the initial monomer concentrations between 0.3 and 1 M and temperatures between -65° and $+5^{\circ}\text{C}$, $\Delta H_{\text{ss}}^{\circ} = -3.6 \pm 0.3$ kcal mole $^{-1}$, $\Delta S_{\text{ss}}^{\circ} = -11.5 \pm 1.5$ cal deg $^{-1}$ mole $^{-1}$; for the 1 M solution the ceiling temperature is $+27^{\circ}\text{C}$. The only product obtainable from the attempted polymerization of 1,3-dioxan was a mixture of crystalline cyclic dimer and trimer.

FOLLOWING on from our study of the polymerization of 1,3-dioxolan¹, in which we investigated the structure of the polymer formed by catalysis with perchloric acid and the thermodynamics of its formation, we have carried out similar work with 1,3-dioxepan.

The polymerization of this monomer was first reported by Hill and Carothers² and although there is a considerable Patent literature on the subject, no fundamental studies of the polymer structure appear to have been made. The first thermodynamic information on the polymerization, which is an equilibrium reaction, came from the semi-empirical calculation of $\Delta H_{\text{gg}} = -4.7$ kcal mole $^{-1}$ by Skuratov and his co-workers³. A brief exploratory study of the monomer-polymer equilibrium of this, and some related compounds was made by Strepikheev and Volokhina⁴. For the polymerization of 1,3-dioxepan in benzene by boronfluoride etherate values for $\Delta H^{\circ} = -3.2 \pm 0.5$ kcal mole $^{-1}$, and $\Delta S^{\circ} = -9.3 \pm 1.4$ cal mole $^{-1}$ deg $^{-1}$, have been reported⁵, which are in good agreement with our results.

EXPERIMENTAL

Materials

1,3-Dioxepan—This monomer was prepared as described⁶. The fraction of b.pt 116° to 118°C at 757 torr was redistilled on a 90 cm column with a reflux ratio of 5:1, giving a product of b.pt 120°C at 753 torr. Analysis by gas-liquid chromatography showed as the only impurity 10^{-2} vol. % of tetrahydrofuran (THF). A second batch was distilled with a reflux ratio 50:1 and had a THF content of 2×10^{-3} vol. %. This difference in purity between the two batches had no effect on the experiments reported here, but it did affect the kinetics which will be discussed subsequently. The monomer was stored over lithium aluminium hydride under its own vapour pressure in a reservoir attached to the vacuum line and reaction vessel.

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Solvent and catalyst—Methylene dichloride was purified by standard methods and stored over phosphorus pentoxide in a reservoir attached to the vacuum line. The only detectable impurity was *ca.* 10^{-2} vol. % of chloroform. Anhydrous perchloric acid and solutions of it in methylene dichloride were prepared as described⁷.

Apparatus and procedure

All experiments were carried out in our adiabatic reaction calorimeter under vacuum, as described¹. The isolation of polymer and analytical techniques followed very closely those used by us previously¹. From kinetic measurements we deduced that the concentration of residual water in the reaction mixtures was about 10^{-4} M. The concentrations of monomer used were in the range 0.3 to 1.0 M and those of perchloric acid (0.2 to 10×10^{-4} M); the temperature range was -65° to 5° C.

Unless otherwise stated, all DP's are number-average values obtained with a vapour pressure osmometer.

RESULTS AND CONCLUSIONS

Nature of the reaction

The polymerization of 1,3-dioxepan by anhydrous perchloric acid is a first-order reaction, which is very much faster than that of 1,3-dioxolan under the same conditions. Like that of dioxolan it goes to equilibrium. The depolymerization is a clean reaction, no compounds other than monomer and solvent being detectable by gas-liquid chromatography after a polymer had been completely depolymerized by raising the temperature of the reaction mixture above the ceiling temperature.

During polymerization the DP goes through a maximum, but once equilibrium conversion has been attained, the DP does not change for at least the following two hours (-20° C). The electrical conductivity of the reaction mixture also did not change during that time, which shows that the viscosity, and therefore the weight-average DP, as well as the number-average DP, remained constant.

The polymers, especially those formed at the higher temperatures, contained appreciable quantities of a crystalline compound. This had a m.pt of 90° to 92° C and was identified as a dimer. The presence of this and of the whole range of oligomers in considerable quantities, even in a polymer made at -40° C, results in a very skew molecular weight distribution, so that this particular polymer had a DP of 70, but an intrinsic viscosity of 5.1 dl g^{-1} (benzene solution at 25° C).

As the polymer is very sensitive to both oxidative and acid-catalysed degradation, we did not succeed in fractionating it, except for isolating the crystalline dimer by vacuum sublimation.

Structure of the polymer

The proton magnetic resonance (p.m.r.) spectra (solution in carbon tetrachloride) of monomer, dimer and polymer are shown in *Table 1*. This information shows clearly that neither the dimer nor the polymer contain end-groups and that they must therefore be cyclic. Nor did the infra-red spectra give any indication of end-groups. Moreover, the p.m.r.

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spectra show that the polymers consist of regular sequences of $-(\text{CH}_2)_4-\text{O}-\text{CH}_2-\text{O}-$ units. The regularity of the enchainment is also proved by our finding that the solution after depolymerization contained no organic constituent other than monomer and solvent.

The propagation mechanism

Our structural findings allow us to generalize the ring-expansion propagation mechanism that we proposed for the polymerization of 1,3-dioxolan

Table 1. The p.m.r. spectra of 1,3-dioxepan, its dimer and polymers, and of 1,3-dioxan and its oligomers

DP	Peak position (τ)			
	1,3-Dioxepan			
1 (monomer)	5.34*	6.31†	8.35‡	
2	5.46*	6.50†	8.31‡	
6§	5.44	6.51	8.37	
70§	5.44	6.51	8.37	
Peak-area ratio	1	2	2	
Position of protons	2	4 and 7	5 and 6	
	1,3-Dioxan			
1 (monomer)	5.18*	6.1†	8.25‡	
2:2 to 2:6	5.4*	6.28†	8.25‡	
Peak-area ratio	1	2	1	
Position of protons	2	4 and 6	5	

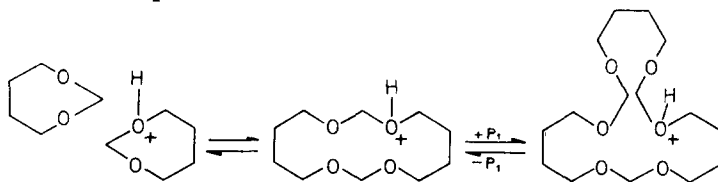
*No fine structure.

†Triplet.

‡Quintuplet.

§The peaks were broad and the fine structure was not resolved. Even when the spectra were run at the highest sensitivity, no other peaks were found.

to that of 1,3-dioxepan

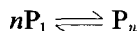


The corollary to the ring-expansion growth reaction is a 'pinching off' of cyclic oligomers as the depolymeration mechanism.

Thermodynamics of polymerization

The relevant results are shown in Table 2 and Figures 1 and 2. Figure 1 shows that ΔT , and therefore also the heat of polymerization, are independent of the monomer concentration (since the number of moles polymerized is a function of this) and therefore we can take ΔH (measured) = ΔH_{ss}^0 . From the electrical calibration of our calorimeter we thus found $\Delta H_{ss}^0 = -3.7 \pm 0.2$ kcal mole⁻¹. From two depolymerizations in the calorimeter we obtained $\Delta H_{ss}^0 = +3.0 \pm 0.4$ kcal mole⁻¹.

The equilibrium constant K for the reaction



we calculated by Tobolsky's equation⁸

$$K = (DP - 1) / DP \cdot m_0$$

where DP is the number average DP and m_e is the equilibrium concentration of monomer.

The van't Hoff plot of the results in *Table 2* gave us $\Delta H_{ss}^0 = -3.5 \pm 0.3$ kcal mole⁻¹; this also showed that there is no significant variation of ΔH_{ss}^0

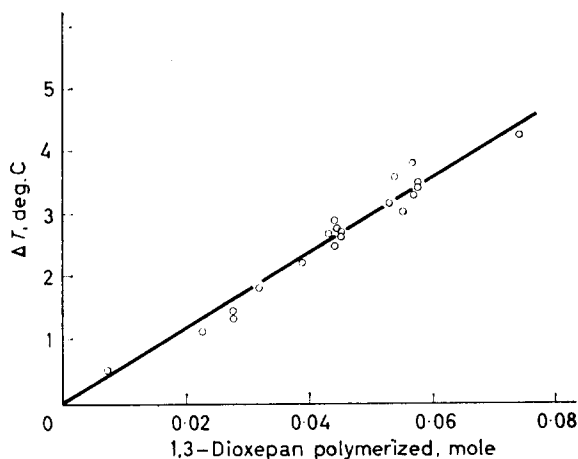


Figure 1—Temperature rise ΔT during polymerization as function of number of moles of 1,3-dioxepan polymerized

with temperature. From the plot of ΔG_{ss}^0 against temperature (*Figure 2*) we obtained $\Delta S_{ss}^0 = -11.7 \pm 1.5$ cal deg⁻¹ mole⁻¹ and ΔS_{ss}^0 also seems to be invariant with temperature.

From *Figure 2* we find the standard ceiling temperature T_c^0 at which $\Delta G_{ss}^0 = 0$ for the 1 M solution (strictly, the ideal 1 M solution) to be +27°C.

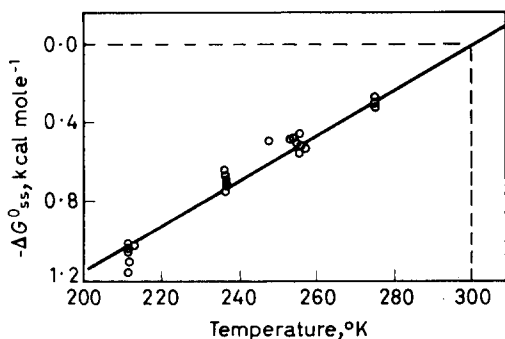


Figure 2—Graphical determination of standard ceiling temperature

The value calculated from our H_{ss}^0 and ΔS_{ss}^0 is $T_c^0 = +26^\circ\text{C}$. Under our conditions departures from ideal behaviour seem to be unimportant.

Oligomerization of 1,3-dioxan (Experiments by Mr F. R. Jones)

This was an exploratory study with 1,3-dioxan covering the temperature

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range 0° to -78°C, with monomer concentrations ranging from bulk monomer (11.7 M) to 1 M (solvent methylene dichloride) and with about 10⁻² M perchloric acid. It showed that the only product formed is a mixture of crystalline dimer and trimer. The DP of the mixture ranged

Table 2. Results for polymerization of 1,3-dioxepan

1	Run No.	148	149	150	153	155	156
2	Final temp. °C	-62	-61	-62	-62	-62	-62
3	[HClO ₄] (10 ⁴ M)	4.1	5.7	7.3	3.0	5.6	5.2
4	m ₀ (M)*	0.60	0.60	0.60	0.60	0.60	0.60
5	m _e (M)	0.07	0.08	0.05	0.07	0.08	0.08
6	No. of moles polymerized	0.057	0.056	0.053	0.058	0.057	0.057
7	ΔT (deg. C)†	3.3	3.8	3.6	3.5	3.7	3.5
8	DP	21.6	10.7	8.3	11.2	12.6	11.0
9	K (M ⁻¹)	14.24	11.70	16.50	12.22	11.50	11.72
10	-ΔG _{ss} ⁰ (cal mole ⁻¹)	1114	1036	1175	1050	1023	1032
1	Run No.	136	137	138	139	144	146
2	Final temp. °C	-37	-37	-37	-37	-37	-37
3	[HClO ₄] (10 ⁴ M)	11.5	1.6	1.2	1.0	5.0	4.0
4	m ₀ (M)*	0.06	0.60	0.60	0.60	0.60	0.60
5	m _e (M)	0.21	0.19	0.20	0.21	0.20	0.21
6	No. of moles polymerized	0.043	0.045	0.044	0.042	0.044	0.043
7	ΔT (deg. C)†	—	2.7	2.5	—	2.9	2.7
8	DP	6.5	11.0	10.8	14.8	7.6	7.1
9	K (M ⁻¹)	4.00	4.80	4.54	4.40	4.30	4.11
10	-ΔG _{ss} ⁰ (cal mole ⁻¹)	649	732	710	692	681	662
1	Run No.	154	143‡	165	163	160	161
2	Final temp. °C	-37	-25	-19	-18	-17	-17
3	[HClO ₄] (10 ⁴ M)	1.6	10.4	2.06	2.1	1.4	2.6
4	m ₀ (M)*	0.60	0.60	0.50	0.60	0.80	0.80
5	m _e (M)	0.19	0.28	0.32	0.31	0.30	0.32
6	No. of moles polymerized	0.045	—	0.023	0.032	0.055	0.053
7	ΔT (deg. C)†	2.6	2.7	1.1	1.8	3.0	2.9
8	DP	7.8	4.1	5.5	6.1	9.4	9.2
9	K (M ⁻¹)	4.54	2.70	2.60	2.70	2.94	2.76
10	-ΔG _{ss} ⁰ (cal mole ⁻¹)	710	484	477	500	550	518
1	Run No.	162	185	171	172	173	
2	Final temp. °C	-16	-17	+2	+2	+2	
3	[HClO ₄] (10 ⁴ M)	2.1	3.8	2.4	1.5	0.9	
4	m ₀ (M)*	1.00	0.35	0.80	0.80	0.80	
5	m _e (M)	0.33	0.28	0.48	0.49	0.47	
6	No. of moles polymerized	0.074	0.007	0.035	0.034	0.035	
7	ΔT (deg. C)†	4.2	0.5	1.9	1.9	—	
8	DP	12.7	3.3	6.3	5.2	5.4	
9	K (M ⁻¹)	2.80	2.43	1.70	1.64	1.70	
10	-ΔG _{ss} ⁰ (cal mole ⁻¹)	525	453	304	274	304	

*m₀ is initial monomer concentration.

†ΔT is temperature rise during polymerization.

‡Reaction 143 was carried out at -40°C, but was killed at -25°C.

from 2.2 to 2.6, it had two melting points, at 86° to 88°C and 101.5° to 102.5°C, and we did not succeed in separating the components. The p.m.r. spectrum of the mixture showed no end-groups of any kind (Table 1). We conclude that the oligomers are cyclic and that they are formed by the same ring-expansion mechanism as the macrocyclic

oligomers and polymers of 1,3-dioxolan and 1,3-dioxepan. The oligomers were only formed under those conditions under which they could crystallize from the reaction mixture; we could never recover them from the solution, presumably because their equilibrium concentration was too low. We also obtained the cyclic dimers by using phosphorus pentafluoride gas as a catalyst. In these experiments occasional and irreproducible traces of oily, coloured, material of DP greater than three were found. Those of our results that may be of use to anyone wishing to study this oligomerization in more detail are summarized in *Table 3*.

Table 3. Oligomerization of 1,3-dioxan in methylene dichloride

m_0^* , M	10^2 [HClO ₄], M	Temp., °C	Time, h	Y, %
4.7	7.8	-78	456	0
4.7	7.8	-40	48	0
9.4	22.0	-40	48	32
10.6	1.2	-39	0.4	0.5
10.5	0.98	-39	0.5	6.4
10.3	1.2	-39	1.0	10
10.5	1.07	-39	2.0	56
11.0	0.7	-39	20	98
10.0	1.45	-35	20	37
†	1.6	+35	21	1

* m_0 is the initial monomer concentration, Y is the weight per cent yield of oligomers.

† Depolymerization of 3.74 base-molar solution.

Discussion

The thermodynamic results, together with those obtained earlier for 1,3-dioxolan by us¹ are summarized in *Table 4*. We note first the good agreement between the ΔH_{ss}^0 values obtained from calorimetry and from the variation of K with temperature. Comparison of the enthalpy values shows the expected trend with increasing ring size. We confirmed the well

Table 4. Thermodynamic constants for the equilibrium polymerization of 1,3-dioxolan and 1,3-dioxepan in methylene dichloride

	1,3-Dioxolan	1,3-Dioxepan
ΔH_{ss}^0 (kcal/mole)		
Calorim., depolym.	5.2 ± 0.6	3.0 ± 0.4
Calorim., polym.	-5.2 ± 0.1	-3.7 ± 0.2
van't Hoff, polym.	-5.1 ± 0.2	-3.5 ± 0.3
Best value	-5.1 ± 0.2	-3.6 ± 0.3
ΔS_{ss}^0 (cal deg ⁻¹ mole ⁻¹)	-18.6 ± 1.2	-11.5 ± 1.5
T_c^0 ($\Delta G_{ss}^0 = 0$) (°C)	1.0	27.0

known fact that 1,3-dioxan does not form polymers under any of the usual conditions, and found that even the crystalline dimer and trimer could only be formed at very high monomer concentrations and only when they could crystallize from the reaction mixture. This means that for this monomer ΔH_{ss}^0 even for the oligomerization must be insufficiently negative to set off the loss of entropy, and that the dimer and trimer can only be formed when their latent heat of crystallization, L_c , makes the enthalpy change $\Delta H_{sc}^0 = \Delta H_{ss}^0 - |L_c|$ sufficiently negative.

As far as the entropy values are concerned, we note that ΔS_{ss}^0 (dioxolan) $-\Delta S_{ss}^0$ (dioxepan) = -7 cal deg $^{-1}$ mole $^{-1}$, which is in fair agreement with the difference ΔS_{ic}^0 (5-ring) $-\Delta S_{ic}^0$ (7-ring) = -9.5 cal deg $^{-1}$ mole $^{-1}$ calculated for the (hypothetical) polymerization of cyclic hydrocarbons⁹.

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