Equilibrium polymerization of thioacetone*

During the course of our work on the bond energy scheme for monomers and polymers[1] extended to sulphur compounds (Part VI), an interesting paper by Burnop and Latham[2] on polythioacetone was observed. Heats and entropies of polymerization of thioacetone (and acetone) in this paper at Table 8, calculated by these authors on the basis of $E_{(C=S)}$ = 110 kcal/mole and other bond-energy schemes and correlation procedures of their choice, seem to be rather unrealistic; for example: $-\Delta H_p(gc)$ = 135.3 kcal/mole, $\Delta S_p(gc)$ = 144 e.u. and the corresponding ceiling temperature defined (?) as $\Delta H/\Delta S$ = 940K for equilibrium polymerization of thioacetone.

The $E_{(C=S)}$ = 124.3 kcal/mole in our generalized bond energy scheme (C, H, X, O and S) is based on $\Delta H_f^0(g)$ = 24 ± 2 kcal/mole of thioformaldehyde determined by Jones *et al.*[3]. This value and the corresponding ΔH_f^0(C=S) = + 27.6 kcal/mole fits in excellently with other bonds in our work and also gives a reasonable estimate of the heat of polymerization of thioacetone as $\Delta H_p^0(gg)$ = −7.7 kcal/mole, less strain energy (if any, in the polymer) of the type: 1–3 interaction $[C_Q-C-C_Q]$ = +5.3 kcal/mole as for polyisobutylene or $[C_Q-O-C_Q]$ = +9.4 kcal/mole for polyacetone, where C_Q is the tertiary carbon atom with two methyl groups [see part II and V of reference 1]. The heat of polymerization, $\Delta H_p^0\,(lc)$ of thiocetone ought to be certainly less (numerically) than 7.7 kcal/mole.

We reexamined the experimental data of Burnop and Latham on equilibrium, monomer-polymer composition from their 1 g.-sealed tube experiments at various temperatures, accepting that equilibrium was established in the 1 h period allowed by these authors. The experimental data as interpolated from their Figure 8 are shown in the following table:

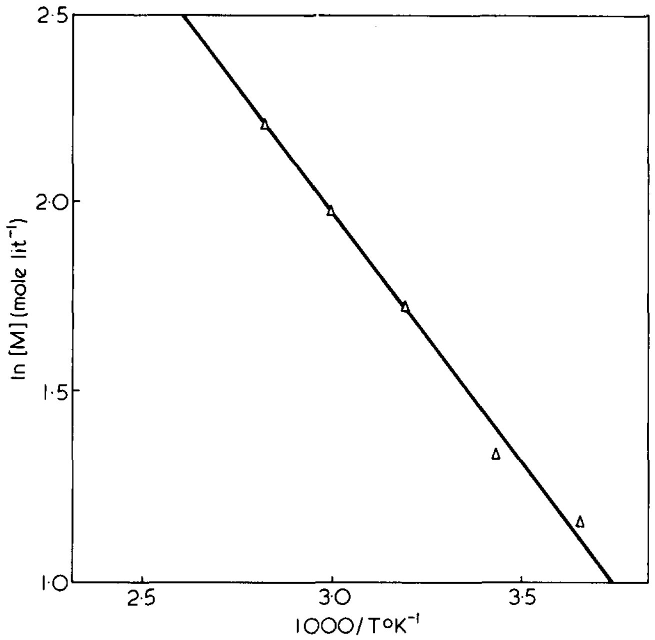
The simple thermodynamic equation for reversible polymerization relating the equilibrium monomer concentration $[M]$, at temperature T_e, to the equilibrium temperature T_e is given by Dainton and Ivin[4] as follows:

$$T_e = \frac{\Delta H}{\Delta S + R\cdot\ln[M]}$$

Table 1 Experimental data of Burnop and Latham[2] on equilibrium polymerization of thioacetone

Temperature T°C	Equilibrium composition % polymer	Equilibrium Monomer Concentration 10³/T(K)	g./1.1$\dot{1}$cm³	mol/l	ln[M]
0	74	3.663	0.26^a	3.162^a	1.152
18	69	3.436	0.31	3.770	1.327
40	54	3.195	0.46	5.595	1.722
60	41	3.000	0.59	7.176	1.971
80	26	2.883	0.74	9.000	2.197

[a] The volume occupied by 1 g. monomer, of density 0.9 assumed for thioacetone, is 1.11111 cm³. [M] in mole/l is calculated accordingly, in column 5 above. The density of monomer is estimated as 0.9 from correlation of densities of oxygen compounds and identical sulphur analogues (e.g. furan-thiophene, 2,5-dimethyloxazole and thiazole, etc.) and adding the incremental value (=0.12) for sulphur substitution in acetone: d^{25} = 0.78. From the available polymer density: 1.21[2], the molar volume change on polymerization: ΔV_p^0 (lc) would work out to about 21 cm³



or

$$\ln[M] = (\Delta H/R)\frac{1}{T} - (\Delta S/R)$$

A plot of ln[*M*] vs. 1/*T* of experimental data of *Table 1* gives a good linear fit which is shown in *Figure 1*. Least Squares treatment of the plot gives the following values for the slope and intercept: slope = (−1.301 ± 0.16) x 10³ and intercept = 5.87 ± 0.5 from which the following values are derived:

$$\Delta H_p^0\,(lc) = -2.59 \pm 0.32 \text{ kcal/mole}$$

$$\Delta S_p^0\,(lc) = -11.7 \pm 1.0 \text{ e.u.}$$

and $T_c = \Delta H/\Delta S$ = 221K, the ceiling temperature for unit monomer concentration, i.e. 91.8% polymer. The 1–3 interaction, strain energy in polythioacetone is likely to be negligible owing to the wider separation of the two crowding $C(CH_3)_2$ groups by a sulphur atom with larger atomic radius: 1.0 Å as compared to carbon: 0.77 Å in polyisobutylene or oxygen: 0.66 Å in polyacetone. Consequently our bond-energy-wise calculated heat of polymerization truly represents: $\Delta H_p^0(gg)$ = −7.7 kcal/mole and in good agreement with $\Delta H_p^0(lc)$ as calculated above from the equilibrium polymerization of thioacetone.

R. M. Joshi
National Chemical Laboratory,
Poona, India 411008
(Received 30 October 1978)
* *NCL Communication No. 2362*

References

1 Joshi, R. M. *J. Macromol. Sci. -Chem.*, 1975, A9(8), 1309 and previous work (loc.cit)
2 Burnop, V. C. E. and Latham, K. G. *Polymer* 1967, 8, 589
3 Jones, A. and Lossing, F. P. *J. Phys. Chem.* 1967, 71, 4111
4 Dainton, F. S. and Ivin, K. J. *Quart. Revs. (Lond.)*, 1958, 12, 61
See also Ivin, K. J. and Leonard, J. *Polymer* 1965, 6, 621

0032–3861/79/030394–01$02.00