Kinetics of the Base-Catalyzed Reactions of Cyclo-octameric and Catenapolymeric Sulfur with Dithiol

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Synopsis

The base-catalyzed sulfur-1,2-ethanedithiol reactions appear to follow pseudo first-order kinetics as determined by TGA. The activation energy has been determined to be 26.1 kcal/mol with either cyclo-octameric or catenapolymeric sulfur.

INTRODUCTION

The use of cyclo-octameric and catenapolymeric sulfur in vulcanization is well known. The latter, the insoluble allotrope of sulfur, is superior to the former in regard to sulfur blooming.[1] The reactions of liquid S_8 with hydrogen sulfide and various p-substituted thiophenols have been investigated in the temperature range 130–160°C and a free-radical mechanism has been proposed.[2,3] Thiols can be oxidized to monosulfides by an amine catalyst at elevated temperatures (100 to 230°C).[4] But thiols can be oxidized by sulfur to polysulfides at lower temperatures (20 to 50°C) in the presence of an amine catalyst.[5,6] Polymeric sulfur is fairly stable to depolymerization at temperatures below about 90°C.[7] The kinetic behavior of cyclo-octameric and catenapolymeric sulfur in the low-temperature base-catalyzed reactions with dithiol forming polymeric polysulfides has been investigated in the present study.

EXPERIMENTAL

Cyclo-octameric sulfur (S_8) is the orthorhombic sulfur of 99.8% purity obtained from the Fisher Scientific Co. and used without further purification. Catena-polymeric sulfur (S_ω) is Regular Crystex of 99.5% purity obtained from Stauffer Chemical Co. after extracting the 10% S_8 present in the commercial product with CS_2. The molecular weight of S_ω is (1 to 3) $\times 10^5$.[1] Crystex also has a stabilizer to retard depolymerization, which is suggested to be 0.2 wt-% dicylopentadiene.[1,8] 1,2-Ethanedithiol (bp 144°C) obtained from Aldrich and diethylamine (bp 55°C) obtained from Fisher are purified by distillation.
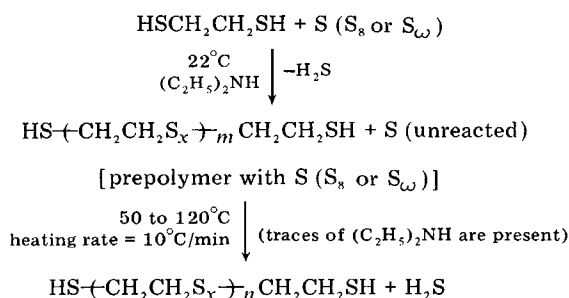
When 1,2-ethanedithiol is mechanically mixed with S_8 and S_ω, both in the form of fine powders, no H_2S evolution is observed at ambient temperature (about 22°C). As soon as a catalytic amount of $(C_2H_5)_2NH$ is added with mixing, a large evolution of H_2S is observed in both cases. The viscosity of the mixtures increases rapidly, and in about 5 min solid products are obtained. The starting compositions of S, $HSCH_2CH_2SH$, and $(C_2H_5)_2NH$ are 5 g, 9.79 g, and 10 μl, respectively, which gives a relative composition of 3 g-atom, 2 moles, and 2×10^{-3} moles, respectively. The reaction is continued for about 18 hr, at which point

no H_2S is detected by moist lead acetate paper. These compositions are then ground to a powder. TLC studies on the CS_2 extracts of these powders using n-heptane as the eluent shows that the sample made with S_8 contains unreacted S_8, whereas that made with S_ω contains no S_8 but is expected to contain unreacted S_ω (S_ω does not dissolve in CS_2). These two samples will be called "prepolymer with S_8" and "prepolymer with S_ω," respectively. Both samples begin melting (vusual capillary method) near 90°C. Molecular weights of the polymeric polysulfides could not be determined because of their insolubility in common solvents.

Within a few hours after their preparation, these samples are placed in platinum crucibles for thermogravimetric analysis (TGA) to evaluate the kinetic parameters of the base-catalyzed sulfur–thiol reaction. The weight loss is due to the evolution of H_2S, which is confirmed by its reaction with moist lead acetate paper. Sample weights of about 30 mg and a heating rate of 10°C/min have been employed using the DuPont-990 thermal analyzer attached with a DuPont 951 thermogravimetric analyzer in both a nitrogen and an air atmosphere.

RESULTS AND DISCUSSION

The base-catalyzed reaction of sulfur (S_8 and S_ω) with $HSCH_2CH_2SH$ can be represented by the following scheme:

$$HSCH_2CH_2SH + S\ (S_8\ or\ S_\omega)$$

$$\underset{(C_2H_5)_2NH}{\overset{22°C}{\Big\downarrow}} -H_2S$$

$$HS{-}(CH_2CH_2S_x)_m\,CH_2CH_2SH + S\ (unreacted)$$

$$[prepolymer\ with\ S\ (S_8\ or\ S_\omega)]$$

$$\underset{heating\ rate\ =\ 10°C/min}{\overset{50\ to\ 120°C}{\Big\downarrow}}\ (traces\ of\ (C_2H_5)_2NH\ are\ present)$$

$$HS{-}(CH_2CH_2S_x)_n\,CH_2CH_2SH + H_2S$$

where $n > m$; and x, the average sulfur rank, may vary with conversion. The first step shown above is extremely rapid. The kinetic parameters that are determined in the present study are for the second step where the reaction rate is measurable because the concentration of the thiol endgroups is relatively low.

TGA has come into wide use for evaluating kinetic parameters.[9-11] The method of Horowitz and Metzger is simple and has been used here.[10] This method shows that the TGA trace for a first-order reaction can be easily analyzed with the help of the following set of equations:

$$\ln \ln \frac{W_i - W_f}{W - W_f} = \frac{E\theta}{RT_S{}^2}$$

provided $\theta/T_S \ll 1$, where T_S is defined as the temperature where

$$\frac{W - W_f}{W_i - W_f} = \frac{1}{e} = 0.368$$

and where the inflection in the TGA trace of a first-order reaction occurs; θ is defined as $\theta = T - T_S$; W_i, W_f, and W are the initial weight, the final weight, and

the weight of the sample at any temperature in the TGA trace, respectively; E is the activation energy, R is the gas constant, and T is absolute temperature.

The TGA traces of the prepolymers with S_8 and S_ω are shown in Figure 1. The linearity of the plot in Figure 2 shows that the reactions follow first-order kinetics in the temperature range of 60 to 100°C. The activation energies are calculated to be 25.9 (taking $T_S = 92°C$) and 26.3 kcal/mol (taking $T_S = 95°C$) for the S_8 and S_ω systems, respectively. Since the average value of T_S, determined from several TGA traces for both the systems, has been found to be 94°C (92 and 95°C being the maximum deviations) for the same slope in Figure 2, the activation energy for both systems can be considered to be the same within experimental error and is about 26.1 kcal/mol. Although the melting points of the systems are near the inflection points, no discontinuity is observed in Figure 2 for the solid-phase and the liquid-phase reactions.
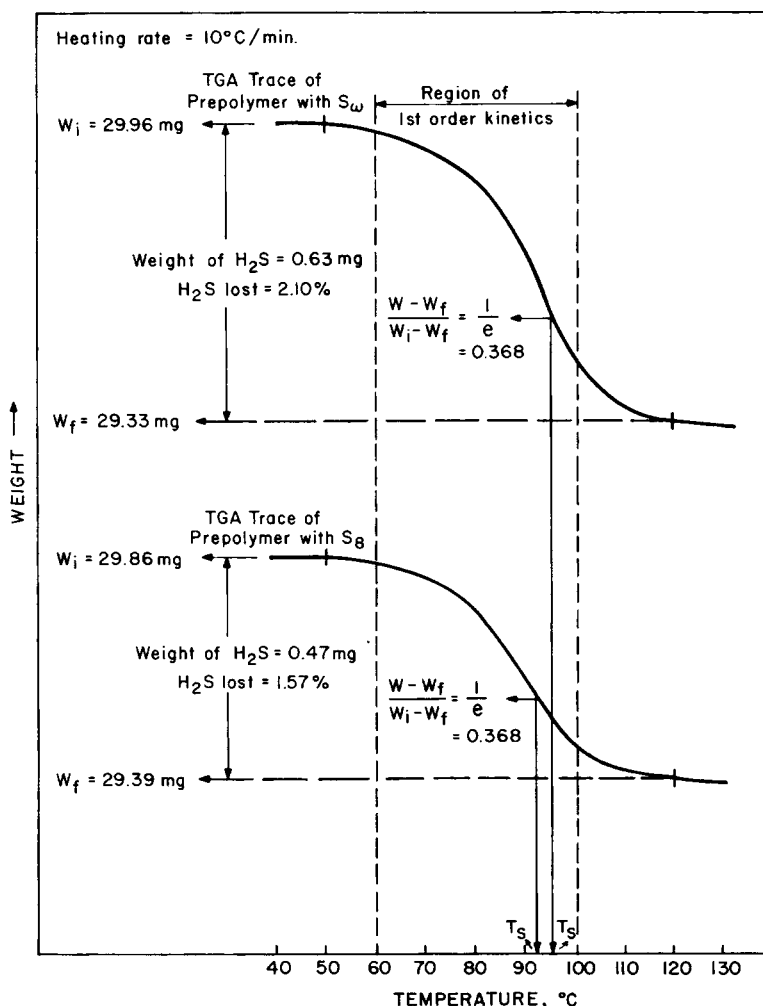

Fig. 1. TGA traces of the prepolymer with S_ω (top) and the prepolymer with S_8 (bottom), each being obtained from the base-catalyzed reaction of 2 moles ethanedithiol with 3 g-atom sulfur at ambient temperature (22°C).
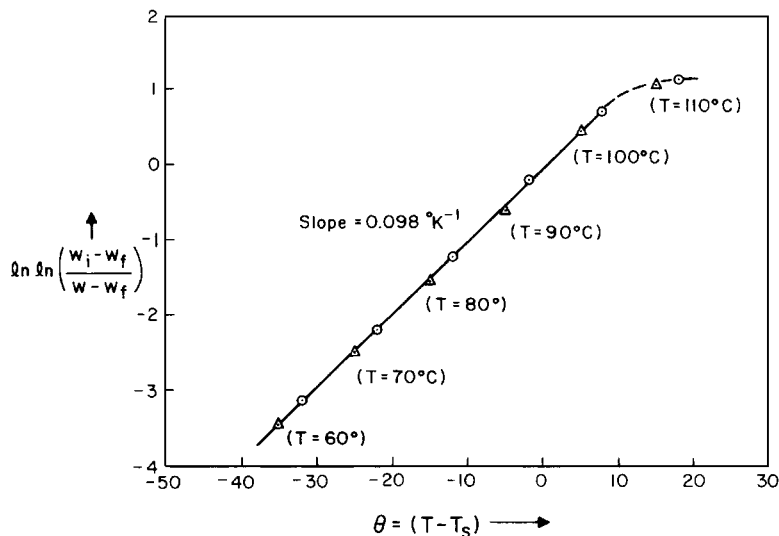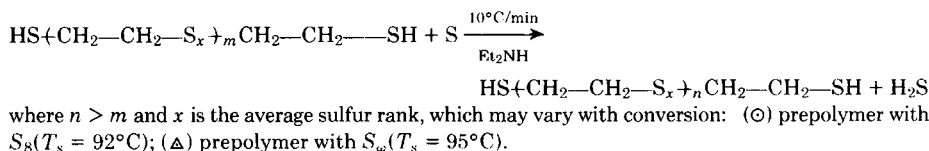
Fig. 2. Plot of $\ln \ln(W_i - W_f)/(W - W_f)$ vs θ for the thermogravimetric analysis of the reaction:

$$HS\text{+}CH_2\text{—}CH_2\text{—}S_x\text{+}_m CH_2\text{—}CH_2\text{——}SH + S \xrightarrow[\text{Et}_2\text{NH}]{10^\circ C/\text{min}}$$

$$HS\text{+}CH_2\text{—}CH_2\text{—}S_x\text{+}_n CH_2\text{—}CH_2\text{—}SH + H_2S$$

where $n > m$ and x is the average sulfur rank, which may vary with conversion: (O) prepolymer with $S_8 (T_x = 92°C)$; ($\triangle$) prepolymer with $S_\omega (T_x = 95°C)$.

Polysulfanes, $RS_x H$, are expected to be formed as intermediates.[3,5] Though such intermediates are reported to be stable under an inert atmosphere,[5] no difference has been observed here between the atmospheres of N_2 and air on reaction kinetics. These intermediates probably break down very readily, giving H_2S and polysulfides, $RS_x R$.

Half-lives of depolymerization of S_ω (Crystex) have been reported to be 50 hr at 76° and 1 hr at 92°C.[7] Therefore, at 120°C both systems are expected to give approximately the same conversion. The quantity of H_2S lost between 50 and 120°C for the S_8 system (1.6 ± 0.1%) has been found to be lower than that for the S_ω system (2.0 ± 0.1%). This would seem to indicate that S_8 reacts a little more efficiently than S_ω at ambient temperature, which may be due either to a difference in the frequency factors or in particle size, if any. Consequently the slightly larger concentration of thiol end groups in the S_ω system gives a slightly larger reaction rate for the S_ω system (3.7 ± 0.2 mol/kg-sec) than the S_8 system (2.8 ± 0.1 mol/kg-sec) at 90°C where both the systems are in the liquid state.

The homolytic dissociation energy of the S–S bond in the S_8 ring, a long-chain polymeric sulfur, and dimethyl tetrasulfide are reported to be about the same, approximately 35 kcal/mol.[12] From the pseudo-second-order rate constants of the uncatalyzed thiophenol–excess sulfur reactions, the activation energy has been reported to be about 32 kcal/mol.[3] This has been attributed to the energy for the homolytic cleavage of the S–S bond in opening the S_8 ring. The observed low value for the activation energy (26.1 kcal/mole) for the base-catalyzed sulfur reactions is comparable to the activation energy of 25.9 kcal/mol obtained by Tobolsky et al. for the S–S bond interchange in crosslinked poly(ethylene tetrasulfide) polymers studied by stress relaxation technique.[13] These bond in-

terchanges may have been catalyzed by base or acid which could be present in trace amounts in the crosslinked polymer because the methods of base-catalyzed polycondensation reaction and coagulation by acidification were used in the synthesis of the polymer.[14,15] Acid catalysis in sulfur reactions has been reported[16] though not investigated in detail. In general, thiol–sulfur reactions are reported to be base catalyzed, probably by a general base-catalyzed path obeying the Bronsted law.[17] The p-aminothiophenol–sulfur reaction is reported to be extremely rapid and overwhelmingly faster than other related reactions.[3] A probable ionic mechanism has been suggested for this reaction, for it deviated from the Hammett-type correlation observed with other p-substituted thiophenol–sulfur reactions for which a free-radical mechanism has been proposed.[3] The observed lower activation energy for the base-catalyzed sulfur reactions appears to agree with the above nature of the p-aminothiophenol–sulfur reaction.

CONCLUSIONS

The base-catalyzed sulfur–dithiol reactions appear to follow pseudo-first-order kinetics as determined by TGA. The activation energies are found to be the same with either cyclo-octameric or catenapolymeric sulfur, which is 26.1 kcal/mol. The observed lower value for the activation energy as compared to about 35 kcal/mol for the homolytic cleavage of the S–S bond in S_8 ring and polymeric sulfur appears to suggest that the cleavage of the S–S bond in the presence of a basic catalyst is ionic in nature.

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