

## Characterization and Polymerization of Thioacetone\*

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### Synopsis

The thioketo and thioenol tautomers of thioacetone have been separated by gas chromatography and characterized by infrared and NMR spectra at low temperatures. The pure thioketo tautomer polymerizes rapidly at room temperature, but the thioenol tautomer does not. At room temperature, the thioenol gradually disappears, probably by tautomerization to the reactive thioketo form, which then polymerizes. Attempts to copolymerize thioacetone with vinyl and diene monomers were not successful.

### INTRODUCTION

Although thioacetone has been the subject of a number of investigations,<sup>1-3</sup> relatively little has been disclosed on the isolation and characterization of the tautomeric forms of thioacetone and their relationship either to the method of synthesis or to polymerization. Several years ago in this laboratory, we investigated the synthesis of high molecular weight polythioketals. Thioacetone received special attention, and several methods of synthesis, isolation, and polymerization were developed. Other investigators who were working in this area concurrently and independently have since reported on the syntheses and polymerization of thioacetone, agreeing substantially with our findings.<sup>1-3</sup>

### RESULTS AND DISCUSSION

In the present investigation, thioacetone was always obtained as a mixture of the thioketone,  $\text{CH}_3\text{CSCH}_3$ , and the thioenol,  $\text{CH}_2=\text{CSHCH}_3$ , although the ratio of tautomers varied widely depending on the synthesis route and conditions. Because of the great propensity of the keto tautomer to polymerize spontaneously even at low temperatures, the equilibrium concentrations of the two tautomers or the time to attain equilibrium was not estimated. It was desired, however, to examine the pure keto tautomer because it was likely the other tautomer, an enethiol, would be an effective transfer agent via its allylic and thiol hydrogens and its presence would preclude formation of high polymer from thioacetone.

\* In honor of C. S. Marvel on the occasion of his 75th birthday.

### Separation of Tautomers

There was evidence that thioacetone could be partially separated into two fractions of somewhat different behavior by vacuum distillation at low temperatures. Each fraction was presumed to be enriched in one of the tautomers, but a nearly quantitative separation appeared unlikely. This did suggest, however, that equilibrium was not rapidly attained. Preliminary experiments with gas chromatography indicated that thioacetone could be separated into two principal components. After numerous trials, a column was developed comprising DC 200 silicone oil on Gas Chrom Z, which was found to be extraordinarily inactive in promoting polymerization and permitted use of 6-ft columns of useful capacity and life. In this way, the thioketo and thienol tautomers were obtained in nearly pure form by gas chromatographic separation at 0°C. It was advantageous to carry out this separation at as low a temperature as possible because thioacetone polymerizes so easily. Very low temperatures were not feasible, however, because of the moderate volatility of thioacetone ( $\text{bp} \sim 70^\circ\text{C}$ ). A reasonable compromise was 0°C, at which temperature polymerization was slow enough in the attenuated state for most of the material to pass through the column unchanged. Two chromatograms are shown in Figure 1 illustrating the wide variation in tautomer ratio that was obtained under different synthesis conditions.

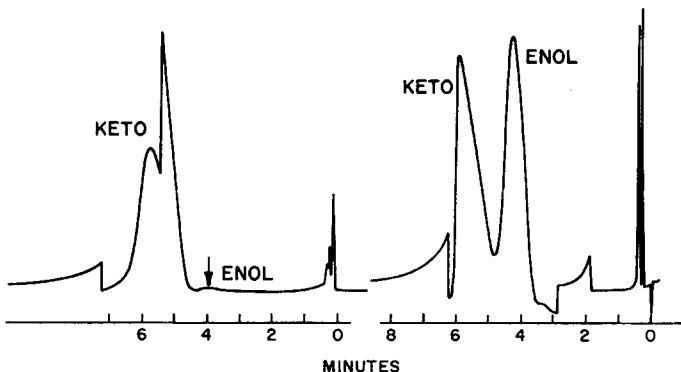


Fig. 1. Gas chromatograms for thioacetone.

### Infrared Characterization

Separation of the tautomers offered the opportunity to obtain the infrared spectra of propanethione and 2-propenethiol, but the small sample size and the great lability of these compounds required the development of a special technique. A cell was designed and constructed that would serve directly as a sample-collecting device and as a low-temperature infrared transmission cell, thus obviating any material transfers. The cell is illustrated in Figure 2. Samples of the tautomers were collected directly at the outlet of the gas chromatographic columns on the cooled surface of a sodium chloride

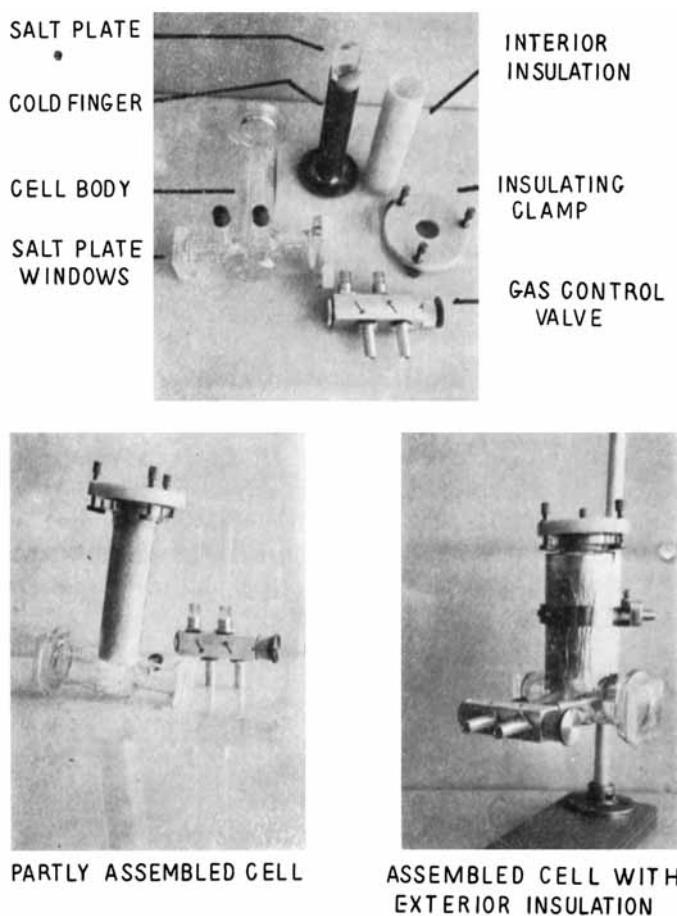


Fig. 2. Infrared cell for direct collection and examination of GC samples.

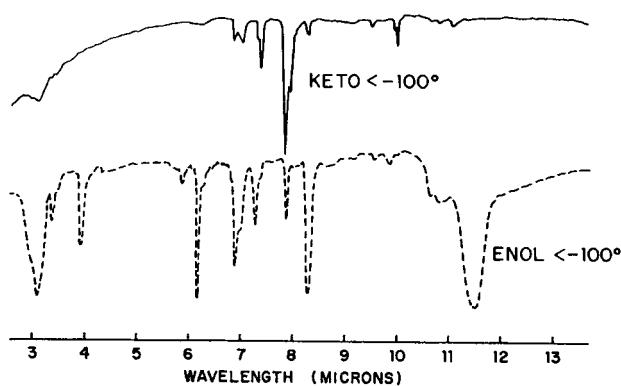


Fig. 3. Infrared spectra of thioacetone tautomers.

plate at  $-100^{\circ}\text{C}$  within the cell, and the spectra were determined immediately at that temperature. In this way, it was possible to retard tautomerization or polymerization, and good spectra of the tautomers were obtained (Fig. 3). It will be noted that the principal characteristic absorptions due to  $-\text{SH}$ ,  $\text{C}=\text{C}$ , and  $=\text{CH}_2$  groups at 3.93, 6.15, and  $11.55\ \mu$  were absent in the spectrum of the keto tautomer. Tentatively, the absorption at  $7.85\ \mu$  is attributed to the  $\text{C}=\text{S}$  group in thioacetone, even though this is at somewhat shorter wavelength than that assigned to  $\text{C}=\text{S}$  absorption in more complex thioketones.<sup>4,5</sup> Neither the stable trimer nor the polymer absorbs at this wavelength.

### NMR Characterization

The NMR spectra of propanethione and 2-propenethiol have proved useful in the study of thioacetone. Figure 4A shows the spectrum, obtained with a Varian HR 60 instrument, of a freshly distilled, enol-rich sample of thioacetone just above the melting point ( $\sim -55^{\circ}\text{C}$ , depending on tautomer ratio). Integration of the spectrum confirmed the expected 2:1:3 ratio for vinyl ( $-4.93\ \text{ppm}$ ), mercapto ( $-3.30\ \text{ppm}$ ), and methyl protons ( $-1.95\ \text{ppm}$ ).

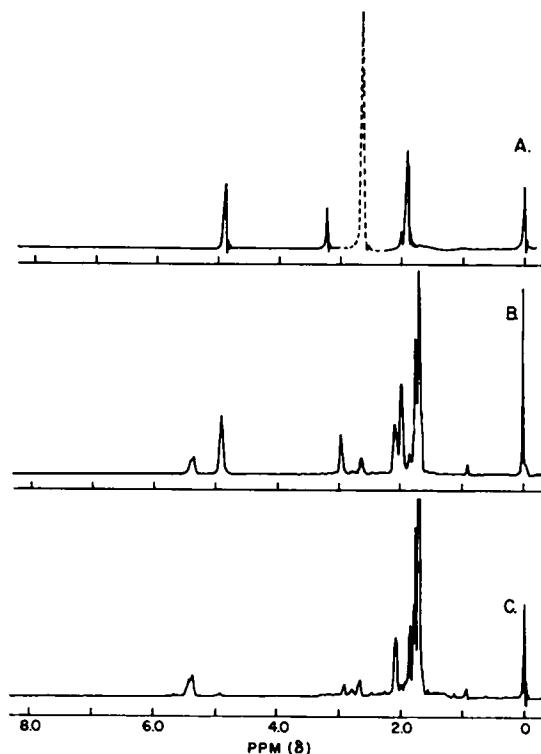


Fig. 4. NMR spectra of enol-rich thioacetone (A) monomer at  $-52^{\circ}\text{C}$ ; (B) after 1 min at room temperature; (C) after 2 days at room temperature.

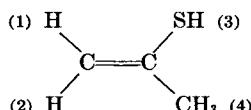
ppm) of the enol. The methyl protons of the keto tautomer absorbed at  $-2.67$  ppm (referred to tetramethylsilane as internal standard) and comprised a little less than 50% of the total area of this spectrum.

The great sensitivity of these compounds is illustrated by the spectrum of Figure 4B, which was obtained immediately after the above sample was warmed to room temperature. The keto tautomer virtually disappeared, and new resonances appeared in the vinyl and methyl regions of the spectrum at about  $-5.4$  ppm and  $-2.09$  ppm, respectively. Much of the enol in this relatively enol-rich sample, however, was still present. After two days at room temperature, the enol tautomer also had largely disappeared (Fig. 4C). When the enol tautomer was present in large proportion, as in this sample, transfer and initiation of new polymer chains would occur frequently enough to permit accumulation of low molecular weight polymer containing vinyl, methyl, and mercaptan endgroups. These are most likely the sources of new vinylic and methyl resonances as well as the residual (SH?) resonance at  $-2.8$  ppm observed in these spectra after polymerization had occurred. The strong resonances that appeared at  $-1.75$  ppm and  $-1.94$  ppm were due to the methyl group protons of propanethione trimer and polymer, respectively.

To assign unequivocally the specific absorptions to the protons of thioacetone, the tautomers were separated by gas chromatography and collected at low temperature directly in NMR sample tubes. The spectrum thus obtained of pure enol, 2-propenethiol, in deuteriochloroform solution at  $-52^\circ\text{C}$  showed the three proton resonances previously assigned to the enol to be present in the required ratio, although the SH resonance was shifted in the solution to about  $-2.8$  ppm. The single resonance assigned to the keto protons was absent. The pure enol tautomer appeared to be fairly stable and failed to change rapidly under these conditions at room temperature, as indicated by the small changes in its spectrum after 1 hr. Gross changes were apparent, however, after two days.

Further confirmation was obtained from the spectrum of pure keto which, as expected, was a single peak. This tautomer was exceedingly labile and polymerized appreciably even at  $-78^\circ\text{C}$  in a few hours or in a few seconds if the temperature was allowed to approach that of the room.

Casual inspection of the spectrum of the enol tautomer suggests that the absorption peaks are all single, unsplit peaks. However, the structure of the enol,



makes it likely that some coupling exists among the protons of this molecule. If SH and  $\text{CH}_3$  were very similar in an electromagnetic sense, then the chemical shift of H (1) and H (2) might be similar and, indeed, this appears to be true here. Attempts were made to resolve the spectrum of thio-

acetone at  $-60^{\circ}\text{C}$ , with moderate success. The vinylic protons, (1) and (2), were separated into a very narrow overlapping pair of multiplets, one of which appeared to be a quadruplet, the other more complex. The band width was less than 8 Hz. The mercapto proton was a closely spaced doublet with a separation of 1.5 Hz at  $-3.28$  ppm, and the methyl protons were split into four closely spaced peaks at about  $-1.98$  ppm with a total band width of  $\sim 5$  Hz. All the couplings were very weak, with none of the constants exceeding 1.5 Hz.

### Control of Tautomer Ratio

Following this development of an assay procedure based on gas chromatography and NMR, it became possible to determine the tautomer ratio in thioacetone and, theoretically, the rate of change of either tautomer to an equilibrium mixture.

The thioketo tautomer could be kept without appreciable change for a short time at temperatures below  $-50^{\circ}\text{C}$ . At higher temperatures, it polymerized quite rapidly. 2-Propenethiol polymerized much more slowly, probably because it must first tautomerize to the keto form. It was quite stable at  $-50^{\circ}\text{C}$  or below.

As ordinarily prepared by low-pressure pyrolysis of hexamethyltrithiane, thioacetone was a mixture containing 85–95% of the thioketo tautomer. Below  $500^{\circ}\text{C}$ , much of the trimer was recovered unchanged. Above  $600^{\circ}\text{C}$ , thioacetone decomposed extensively. Within the range of  $500$ – $600^{\circ}\text{C}$ , the thioketo:thioenol ratio increased with increase in pyrolysis temperature.

Pyrolysis in a tube packed with fresh quartz rings gave a product relatively rich in thioenol tautomer. Use of the tube for a number of successive runs resulted in conditioning such that each successive product was a little richer in the thioketo tautomer up to a maximum of a little over 95%. Relatively large amounts of the thioenol, 2-propenethiol, were obtained by pyrolysis of 2,2-propanedithiol over sodium fluoride pellets at about  $200^{\circ}\text{C}$ . Formation of thioketones by pyrolysis of *gem*-dithiols was studied earlier by Bleisch and Mayer,<sup>6</sup> but they made no mention of thioketo/thioenol tautomerism. In our hands pyrolysis at  $150^{\circ}\text{C}$  gave a deep-red product containing more than 90% of the thioketo form. However, at  $250^{\circ}\text{C}$  more than 50% of the product was the thioenol tautomer. We suggest that the relatively weak C—S and S—H bonds of the *gem*-dithiol group break first at relatively low temperatures to result in high conversions to propane-thione. At higher temperatures the stronger but more numerous C—H bonds become involved, which leads to substantial quantities of 2-propenethiol.

### Polymerization

It was assumed that 2-propenethiol would be an efficient chain-transfer agent for either anionic or free-radical polymerizations. Polymerization by either mechanism of the pure thioketo tautomer in the absence of the

enol should lead to high molecular weight polymer. It was found that initiation of >95% purity propanethione with the triethylborane-diethyl (peroxyethyl)borane redox couple<sup>7</sup> at -50°C gave a product melting at 120–124°C, which is the melting temperature that Burnop and Latham gave for high molecular weight polymer. However, this polymer did not have the toughness and film- and fiber-forming characteristics that would be expected of truly high molecular weight material. Ultraviolet irradiation of the thioketo tautomer gave a somewhat lower melting product that was also weak and brittle. Both polymers appeared to be stable for at least several weeks, which was not observed for polymer prepared from thioacetone containing substantial amounts of thienol.

Initiation of thioacetone composed of more than 95% of the thioketo tautomer by sodium hydride at -60°C led to rapid reaction as indicated by the rapid disappearance of orange-red color and formation of white, solid polymer. This white polythioacetone melted at 119–120°C and had a molecular weight of only 1500. Apparently the concentration of thienol was not sufficiently low to permit high molecular weight polymer in anionic systems, though this product did melt higher than that prepared under similar conditions from high thienol content monomer.

Potassium *tert*-butoxide was also used to initiate polymerization of >95% thioketo thioacetone. The result was a rapid loss of orange color followed by slow formation and precipitation of solid polymer. Unless removed and purified, the solid polymer slowly reverted to form a viscous liquid polymer. Reversibility of base-catalyzed polymerization of thioacetone was noted on a number of occasions. The highest melting point for polymers formed by potassium *tert*-butoxide initiation was 71–73°C. It is likely that the base promotes formation and stabilization of the enol form leading to low molecular weight polymer containing many thiol and vinylic groups.

Though thioacetone polymerized readily in free-radical systems, it did not copolymerize with diene or vinyl monomers. Attempts to copolymerize it with 2,3-dimethylbutadiene, methyl methacrylate, acrylonitrile, vinyl acetate, or styrene led only to thioacetone homopolymer. In this respect, thioacetone differs from thiocarbonyl fluoride, which copolymerizes readily with a large number of vinyl monomers.<sup>7</sup>

## EXPERIMENTAL

### Hexamethyl-s-trithiane and 2,2-Propanedithiol<sup>8,9</sup>

The cyclic trimer was prepared from acetone and hydrogen sulfide as described by Böhme et al.<sup>10</sup> The only modification was reaction at a lower temperature than the 10°C used by Böhme. In addition to the trimer, 2,2-propanedithiol was also obtained as a major product. At -25°C, the *gem*-dithiol comprised about 30–40% of the product mixture. The crude product was decanted from the ZnCl<sub>2</sub> catalyst, dried, and isolated by fractional distillation under reduced pressure. The dithiol was a colorless

liquid, bp 40°C/43 mm,  $n_D^{25}$  1.5068, with an intensely powerful, disagreeable odor. The trithiane distilled at 101°C/5 mm,  $n_D^{25}$  1.5393.

### Thioacetone

**From Hexamethyl-s-trithiane.** Thioacetone was prepared by pyrolyzing hexamethyl-s-trithiane on hot quartz rings under reduced pressure with subsequent quenching of the product as quickly as possible to -78°C.<sup>11</sup> The pyrolysis temperature was fairly critical. Within the pressure range of 5–20 mm, a temperature below about 500°C permitted much of the trimer to survive. Above 650°C, decomposition to simpler compounds became excessive, and allene and hydrogen sulfide became important products. Under favorable conditions, 80% yield of red-orange, clear liquid monomer could be obtained, which could be redistilled quantitatively in a vacuum system.

In a typical pyrolysis, 7 g of hexamethyl-s-trithiane was added dropwise over 1 hr to a vertical, quartz pyrolysis tube (1 × 12 in.) packed with 8-mm sections of quartz tubing and heated to 560°C. The pressure was maintained at 11 mm. The product was collected in a U-trap cooled to -78°C and attached directly to the pyrolysis tube. When the pyrolysis was completed, the red-orange liquid product was distilled at -20°C and under <1 mm pressure to another trap. All distilled except for approximately 1 g of trimer, which had survived the pyrolysis. The distilled monomer (4.8 ml) crystallized to an orange solid at -78°C but melted readily on slight warming. It was easily redistilled in a vacuum system.

**From 2,2-Propanedithiol.** The vapor of 2,2-propanedithiol was passed through a 1-in. diameter quartz tube packed over a length of 9 in. with sodium fluoride pellets heated to 150°C. The pressure was reduced to 11 mm and the product was collected in a Dry Ice-cooled trap and a liquid nitrogen-cooled trap connected in series. From 4.2 ml of the *gem*-dithiol was obtained 1.1 ml (theory, 1.3 ml) of hydrogen sulfide in the liquid nitrogen-cooled trap and a deep-red liquid product in the Dry Ice-cooled trap. The product obtained under these conditions had an unusually strong tendency to polymerize, and as a result only a small amount could be distilled before the remainder had polymerized. After trituration with methanol, the polymer thus isolated was a white solid melting at 112–115°C.

When the pyrolysis temperature was raised to 200°C, under otherwise similar conditions, the product was an orange liquid, in contrast to the deep-red product of pyrolysis at 150°C. However, nearly the stoichiometric amount of hydrogen sulfide was obtained during the pyrolysis as before. Furthermore, the orange product showed no great tendency to polymerize spontaneously at low temperatures. Free-radical initiation at -78°C yielded a solid polymer in greater than 60% yield melting at 90–92°C.

### Polymerization of Thioacetone

Purified thioacetone can be polymerized to a solid polymer reproducibly simply by allowing the monomer to stand at -10 to -20°C for 20–25 hr.

At lower temperatures, the spontaneous polymerization was exceedingly slow, whereas at higher temperatures much liquid polymer was likely to be obtained. Many polymerization initiators have been scouted; of these, free-radical initiators have been most effective in giving solid polymers. Polymers obtained by radical-induced polymerization were very similar to those obtained by spontaneous polymerization but could be obtained in a very much shorter time. For example, it would take many days to get a good yield of polythioacetone by spontaneous polymerization at  $-50^{\circ}\text{C}$ . With radical initiation, this time was reduced to a few minutes.

Selection of free-radical initiators was restricted by the necessity of polymerization at low temperatures. Suitable initiators included photoinitiators and reduction-activated systems.

As Table I indicates, light alone was effective in accelerating the rate of polymerization. Addition of photoinitiators to the system results in a marked increase in polymerization rate. The apparent greater efficiency of ethyl azodiisobutyrate may result from the fact that this compound is a liquid and can thus dissolve in and mix more readily with the cold monomer.

TABLE I  
Photoinitiation at  $-50^{\circ}\text{C}$  ( $>3000 \text{ \AA}$ )

Photoinitiator	Time for solid polymer, hr
None	$>16$
$\alpha,\alpha'$ -Azobisisobutyronitrile	6
Benzoin methyl ether	2
Ethyl azodiisobutyrate	<0.5

Free-radical initiation with the triethylborane (TEB)-oxygen redox system gave rapid polymerization (Table II). Triethylborane alone, without oxygen, was ineffective. Greatest activity and control were obtained when diethyl(peroxyethyl)borane was substituted for oxygen as the oxidizing component.<sup>7</sup>

TABLE II  
Redox Initiation

Initiator	Time for solid polymer, min	Temp, $^{\circ}\text{C}$
TEB	None	$-50$
TEB/ $\text{O}_2$	10	$-80$
TEB/ $\text{O}_2$	30	$-50$
TEBO <sub>2</sub> /TEB	4	$-80$

Other types of initiators were scouted. Acid catalysis appeared to favor trimerization, which proceeded rapidly even at  $-80^{\circ}\text{C}$ , although some solid polymer was obtained by the action of boron trifluoride on solid thioacetone at  $-120^{\circ}\text{C}$ .

Base catalysts resembled free-radical initiators, although dimethylformamide induced polymerization at a very low rate. Stronger bases, for example, tetraethylammonium cyanide, butyllithium, sodium hydride, or potassium *tert*-butoxide, caused rapid polymerization even at -50°C to solid polymers. The polymers obtained were less stable than those from free radicals and changed almost entirely to liquid polymers in 24–48 hr if the catalysts were not neutralized promptly with acetic acid.

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