Structure and Photochemistry of Matrix-isolated Monothioacetylacetone

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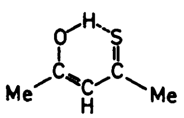
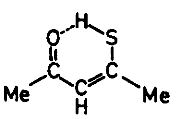
Summary Monothioacetylacetone has been shown, by i.r. spectroscopy of the matrix-isolated species, to consist primarily of two substances which are photointerconvertible; namely the chelated enethiol (*Z*)-4-mercaptopent-3-en-2-one (**2**) and its less stable *s-trans*-conformer (**4**).

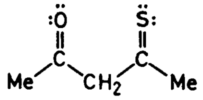
The monothioacetylacetone system (TAA)† is of interest as an analogue of enolizable β-diketones,[1] particularly with respect to the influence of the sulphur atom on kinetic and thermodynamic relations amongst the various stable rotamers and tautomers. TAA can, in principle, exist as the distinct chelates (**1**) and (**2**), the tautomer (**3**), or as



(1)

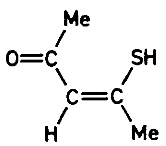


(2)

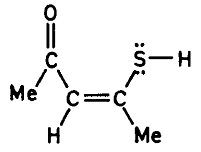


(3)

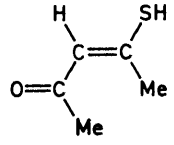
various non-chelated conformational forms of the *E*- and *Z*-isomers (**4**)—(**11**). Published work concerning the composition of this system has been inconclusive;[2—10] thus, there is considerable disagreement regarding the nature and concentration of the species which constitute TAA.



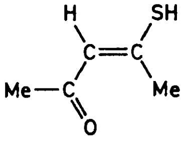
(4)
s-trans-(Z)



(5)
s-cis-(Z)



(6)
s-trans-(E)



(7)
s-cis-(E)

Enethiols

Recently, Duus and Anthonsen have demonstrated the presence, at room temperature, of two species, (A) and (B), which are in thermal equilibrium.[9] The relative concentrations of species (A) and (B) may be altered photochemically [equation (1)] at 95K [10] (2-methylbutane–methylcyclohexane, 5 : 1), where (A) and (B) are thermally stable. Above 130—150K, species (B) reverts to the more stable component (A). Equilibrium is established at $T > 240\text{K}$ where the energy barrier between (A) and (B) is overcome. Based primarily on the calculations of Fabian[7] and on n.m.r. data,[9] the Danish workers have assigned the chelate structures (**1**) and (**2**) to the species (A) and (B), respectively.

$$(\text{A}) \underset{\lambda\ 300\ \text{nm, 95K}}{\overset{\lambda\ 353\ \text{nm, 95K}}{\rightleftarrows}} (\text{B}) \tag{1}$$

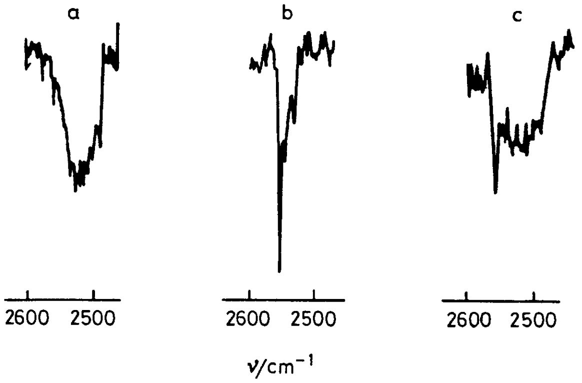


Figure 1. The thiol S–H stretch region of the i.r. spectrum: a, argon-matrix-isolated TAA (M/R 500, *T* 12K, 26 mm); b, after irradiation for 30 min through a 350 nm interference filter; c, after irradiation of argon-matrix-isolated TAA (M/R 500, *T* 12K, 30 mm) through 350 nm (for 20 min) and 300 nm (for 60 min) interference filters. [Note that both compounds (**2**) and (**4**) are present in c.]

Using the matrix-isolation technique,[11,12] we have identified key functional groups in the species (A) and (B) which indicate their structures.‡ TAA matrix-isolated in Ar (M/R 500, 12K, Figure 1a) exhibits a weak absorption at ν 2507 cm^{-1} (not present in the spectrum of S-^{2}H-TAA) which is considerably broader than, and shifted from, typical values (ν 2590—2550 cm^{-1}) observed for 'free' S–H stretches.[13] The signal at ν 2507 cm^{-1} is reasonably ascribed to the chelated enethiol[14] (*Z*)-4-mercaptopent-3-en-2-one (**2**), which is the predominant component (A) of TAA (*vide infra*).

Irradiation of argon-matrix-isolated TAA (λ 350 nm) converted species (A) into (B) (>90%) which gave intense absorptions at ν 1688 and 1577 cm^{-1} (conjugated C=O and C=C) and a sharp absorption at ν 2558 cm^{-1}, characteristic of an S–H stretch (Figure 1b). Irradiation at λ 300 nm reversed the process in the direction of the chelate (**2**) (Figure 1c).§ The photochemical dependence of TAA, monitored by u.v., has been described previously.[10]

The unchelated ('free') S–H stretch at ν 2558 cm^{-1} is clearly incompatible with the enolic structures (**8**)—(**11**). Species (B) is too stable to be the conformer (**5**), which differs from the enethiol (**2**) primarily by rotation around the C–S bond. Since the energy barriers to rotation of the mercapto-group are generally $\leqslant$1—2 kcal mol^{-1} (1 cal = 4·184 J),[15,16] and species (B) only reverts to the chelate (**2**) above 130K, the conformer (**5**) cannot be (B). Species

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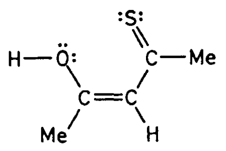
† TAA refers to those species which comprise the monothioacetylacetone system.

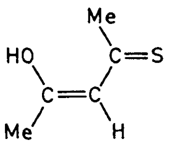
‡ Our matrix-isolated species are identical with those observed by Duus (refs. 8—10) at room temperature, since quenching of a gaseous sample onto a surface maintained at cryogenic temperatures freezes the high-temperature equilibrium (P. Felder and Hs. H. Gunthard, *Chem. Phys. Lett.*, 1979, **30**, 347; *Spectrochim. Acta, Part A*, 1980, **36**, 223).

§ Photochemical reactions were carried out with a 1000 W Hg–Xe lamp. A Displex refrigerator CS 202 (Air Products and Chemicals Inc.) and a Perkin-Elmer 180 Spectrophotometer in the constant I_0 mode were utilized in these studies.



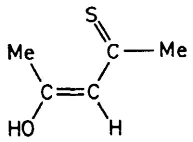
(8)

s-cis-(Z)



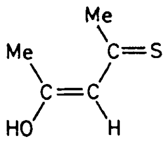
(9)

s-trans-(Z)



(10)

s-cis-(E)



(11)

s-trans-(E)

Enols

(B) is too reactive to be an *E*-isomer of compound (**2**), since Shvo and Belsky have shown that MeSCH=C$(CO_2Me)_2$ [undoubtedly a more labile system than compounds (**6**) or (**7**)] is configurationally stable to rotation about the double bond, at least below 473K.[17]

On the other hand, the remaining alternative, structure (**4**), which differs from compound (**2**) primarily with respect to rotation around the C_2–C_3 bond, is an eminently suitable candidate for species (B). The estimated barrier (*ca.* 8—10 kcal mol^{-1})¶ for the conversion of species (B) into compound (**2**) is only a few kcal mol^{-1} higher than the barrier to rotation around the central C–C single bond in acrolein and methyl vinyl ketone.[18] The small perturbation is to be expected for the weakly interacting mercapto-group.[19]

Photoinduced conformational changes, such as (**2**) → (**4**), are common in the photochemistry of trapped species.[20–24] Furthermore, the analogous acetylacetone system has been reported[25] to undergo a rapid and reversible unimolecular reaction upon nanosecond flash-photolysis at room temperature, which is best interpreted as involving the oxygen analogue of compound (**4**) as the primary photochemical product. Thus, the above interpretation of events in the TAA system is not without precedent.

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¶ This barrier was calculated on the assumption of a half-life for species (B) at 130K of 1—10 min and an *A* factor of 10^{12}—10^{14}.

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