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On photolytic synthesis of sulphur-bearing organic molecules by reacting S or S_2 with the hydrogen end-capped polyyne $C_{10}H_2$

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Abstract: The photolysis of dilute solutions of octacyclosulphur or hexacyclosulphur in n-hexane with 253.6 nm UV radiation produces S and possibly S_2. The 'ring-opening' yields of these sulphur molecules range from 0.2 to 0.7. When the hydrogen end-capped polyyne $C_{10}H_2$ is irradiated in n-hexane, it transforms into unidentified products with a quantum yield of 3×10^{-5}. When octacyclosulphur is added to the solution, the yield rises to 7×10^{-3}. The putative sulphur-bearing product(s) could not be identified. It is suggested that sulphur-bearing molecules might be formed in astronomical settings by reactions of carbon molecules having triple or double C—C bonds with photolytically produced S and/or S_2.

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Introduction

Sulphur-bearing organic compounds such as the amino acids cysteine and methionine are basic constituents of biochemistry. From which classes of compounds and how might they form in astronomical environments? Model theories usually consider reactions between neutral species, ion–atom interactions or ion–molecule reactions (see, for example, Smith *et al.* (1988)). Photolytic processes are considered less frequently, even though the thresholds of $CS_2 \rightarrow CS + S$ and of $OCS \rightarrow CO + S$ are in the near-ultraviolet at 277.8 and 397.3 nm (Lee 1984) and the photolytic dissociation of H_2S yields S_2 (Grim & Greenberg 1987). The present study addresses this issue by investigating a hypothesis of photochemical synthesis involving carbon molecules with triple $C \equiv C$ bonds and sulphur atoms or molecules. Hydrogen end-capped polyyne $C_{10}H_2$ was chosen to represent reactive carbon compounds in part because it can be easily synthesized in organic solvents (Cataldo 2003), in part because $C_{10}H_2$ has a strong absorption band at 252 nm near the 253.6 nm emission line of the ultraviolet lamp and, lastly, because acetylene and some polyacetylenes and/or sulphur are known to occur in interstellar and circumstellar media, in cometary comas, in the atmosphere of the planet Jupiter, on Saturn's largest satellite Titan and on Jupiter's satellite Io (A'Hearn *et al.* 1983; Cernicharo *et al.* 2001; Coustenis *et al.* 1989, 1999; Moses *et al.* 2000; Shindo *et al.* 2003; Thaddeus *et al.* 1998; Vuitton *et al.* 2003). Octacyclosulphur, c-S_8, was chosen as the source for reactive sulphur species. The formulae c-S_n (cyclic) and o-S_n (open) are used to ensure textural distinction between cyclic and open molecular sulphur structures. Octacyclosulphur when exposed in CS_2 to ultraviolet radiation from a high-pressure Hg lamp yields substantial amounts of c-S_6 and c-S_7 plus lesser amounts of c-S_5, c-S_9, c-S_{10} and c-S_{12}, presumably via the unstable open o-S_8 diradical (Strauss & Steudel 1987). The photolysis of c-S_6 in CS_2 yields c-S_8 and c-S_7, and the photolysis of c-S_7 in CS_2 yields c-S_8 and c-S_6 as major products (Strauss & Steudel 1987). The results strongly suggested that significant amounts S and S_2 were also formed. As Strauss and Steudel (1987) did not calibrate their high-pressure Hg lamp, they could not determine photolytic yields of c-S_8 and c-S_6 'destruction' or yields of the respective photolytic products. The photolyses of c-S_8 and c-S_6 in n-hexane are therefore quantitatively studied here with a calibrated low-pressure Hg source. S and S_2 formed by photolysis were used for reaction with $C_{10}H_2$ in n-hexane.

Experiment

$C_{10}H_2$ was obtained by the immersed carbon-arc method (Cataldo 2003) and was purified by high-pressure liquid chromatography (HPLC) on a MetaChem Technologies Inertsil octadecylsylil (ODS; 5 μm; 4.6 × 250 mm) column with n-hexane (95% n-hexane, 5% methylcyclohexane) as mobile phase. Photolyses of $C_{10}H_2$ with and without sulphur were done in n-hexane. Octacyclosulphur was sublimated sulphur that contained a trace of c-S_6 but no detectable c-S_7. Its photolysis was studied in n-hexane and methanol. Weighable amounts of hexacyclosulphur were made by reacting sodiumthiosulfate with hydrochloric acid. The solid product, recrystallized from n-heptane, was c-S_6 with traces of c-S_7 and about 1 mol% c-S_8. Its photolysis was studied in n-hexane.

The solutions for photolysis were placed in a quartz cuvette with a 10 mm light path. The radiation source was an 11SC-1 low-pressure Hg pen-ray lamp, whose strongest ultraviolet lines are at 184.9 and 253.6 nm. As the photolysis rate of $C_{10}H_2$ was relatively slow, the lamp was placed centrally against a 3 mm quartz cuvette that contained an aqueous KBr absorber, which, in turn, was placed against the sample cuvette. The absorber was used to prevent any 184.9 nm radiation from entering the sample. The same geometry was used for calibrations of the 253.6-nm radiation with the potassium ferrioxalate actinometer (Hatchard & Parker 1956). The 253.6-nm photon flux through the cuvette's entry face was $8.8 \pm 0.9 \times 10^{15}$ photons $cm^{-2}\,s^{-1}$. Owing to the dimensions of the cuvette, this was also the number of photons entering 1 cm^3 of solution every second. For the much faster c-S_8 and c-S_6 photolyses, the distance between the sample cuvette and lamp was increased to 38 mm and the KBr absorber was not used. The photon flux was adjusted for the change in distance. Exposure times were controlled with a manual shutter. Aliquots of 0.05 ml were taken for HPLC analysis from each irradiated sample after various exposure times. A series of 'blank' irradiations of neat n-hexane and methanol were also done to check whether detectable products might interfere with analyses of the sulphur species or $C_{10}H_2$. No interference was found.

$C_{10}H_2$ concentrations were monitored with the HPLC system mentioned above. The $C_{10}H_2$ absorptivity from the literature was used (Eastmond *et al.* 1972). Concentrations of c-S_8, c-S_7 and c-S_6 were monitored by HPLC with either a Nacalai Tesque buckyprep (bp) column (4 × 250 mm) with hexanes (86.1% n-hexane, 9.7% methylcyclopentane and 4.2% methylpentanes) as mobile phase or the ODS column with methanol as mobile phase. Owing to peak-overlap of c-S_7 and c-S_8 on the bp-column, the concentrations of c-S_7 and c-S_8 were obtained with a peak-resolving program using absorptions at two different wavelengths. However, when the c-S_8 peak area overwhelmed that of c-S_7, the c-S_7 concentration could not be reliably obtained. The absorptivities of c-S_6 (ε_6) and c-S_8 (ε_8) in n-hexane were determined for this study by HPLC at 234 nm (5642 $dm^3\,mol^{-1}\,cm^{-1}$) and 263 nm (6445 $dm^3\,mol^{-1}\,cm^{-1}$), respectively. The ε_7 value in methylcyclopentane of 5550 $dm^3\,mol^{-1}\,cm^{-1}$ at 255 nm from the literature was used (Steudel *et al.* 1988).

Results and discussion

Solutions of $C_{10}H_2$ with c-S_8 and c-S_6 were stored in the dark and at room temperature for 24 hours to check whether $C_{10}H_2$ reacted measurably with the sulphur-bearing molecules in the absence of radiation. No changes in polyyne or sulphur concentrations were found.

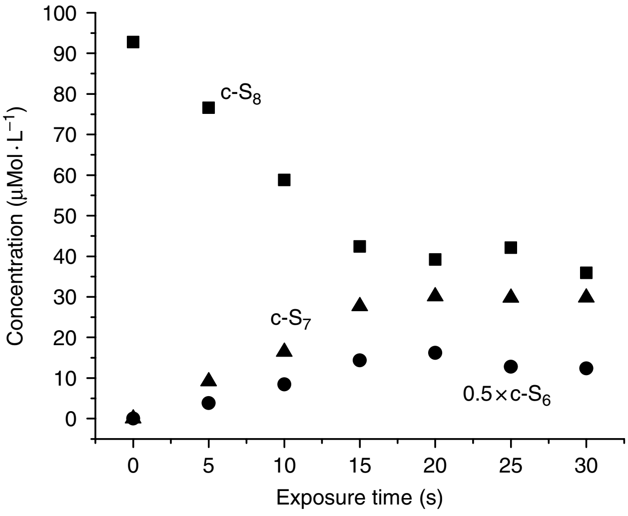
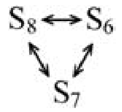


Fig. 1. Photolysis of c-S_8 in methanol: concentration versus exposure time.

Figure 1 shows the photolysis of c-S_8 in methanol. From 0 to 15 s, the concentration of c-S_8 decreases while those of c-S_6 and c-S_7 increase. From 15 to 30 s, the concentrations remain roughly unchanged, but there is a slight and real concentration maximum of c-S_8 near 25 s. Apparently, a quasi-stationary parti-closed photolytic system develops from which sulphur atoms are only lost by the formation of other S_n species such as S, S_2, c-S_5, c-S_9, c-S_{10}, c-S_{12} and the photo-sulphur polymer:



Owing to this 'cycle', quantitative analyses of the functions of Figure 1 and analogous functions from the additional experiments in n-hexane are extremely complex. However, since only one sulphur species is present in solution at the start of the photolysis, its rate of 'destruction' and the rates of formation of its major photolytic products at this time were obtained by differentiation of the respective functions at t_0. Although the total irradiated volumes of solutions were 3 ml, the actual calculations were done for the processes occurring in a 1 cm^3 volume of the irradiated solutions. For every photolysis, normalized yields Φ (normalized to a standard concentration of 1 $\mu mol\,cm^{-3}$) of the 'destruction' of c-S_8 or c-S_6 to assumed open intermediate diradicals or the formation of detectable reaction products were computed with the equation:

$$\Phi = R_0 / C_0 \cdot F \cdot A_0 \qquad (1)$$

R_0 is either the initial destruction rate of c-S_8 or c-S_6, or the initial formation rate of products c-S_6, c-S_7 or c-S_8 in $\mu mol\,cm^{-3}\,s^{-1}$. C_0 is the initial concentration of c-S_8 or c-S_6 in $\mu mol\,cm^{-3}$. F is the number of photons entering the 1 cm^3 reaction volume each second. A_0 is fraction of 253.6-nm photons absorbed by the reactant c-S_8 or c-S_6 molecules at the start of the photolysis. At that time the reaction products do not yet absorb. n-Hexane was essentially 100% transparent

Table 1. *Summary of normalized photolytic yields*

Sulphur species	Solvent	Concentration at t_0 (μM)	Φ_1	Φ_2	Φ_3	Φ_4	Φ_5	A_0
S_8	n-hexane	75.5	0.62			0.34	*a*	0.63
S_8	n-hexane	51.4	0.52			0.37	*a*	0.53
S_8	n-hexane	39.4	0.58			0.34	*a*	0.44
S_6	n-hexane	166		0.47	0.20		0.20	0.67
S_6	n-hexane	109.8		0.52	0.24		0.26	0.53
S_6	n-hexane	66.0		0.54	0.25		0.25	0.36

Notes: $\Phi_1=S_8$ ring-opening to intermediate; $\Phi_2=S_6$ ring-opening to intermediate; $\Phi_3=S_8$ formation; $\Phi_4=S_6$ formation; $\Phi_5=S_7$ formation; $a=\mathrm{d}c_7/\mathrm{d}t$ resulting from small differences of two large numbers, due to peak-overlap, hence not reported.

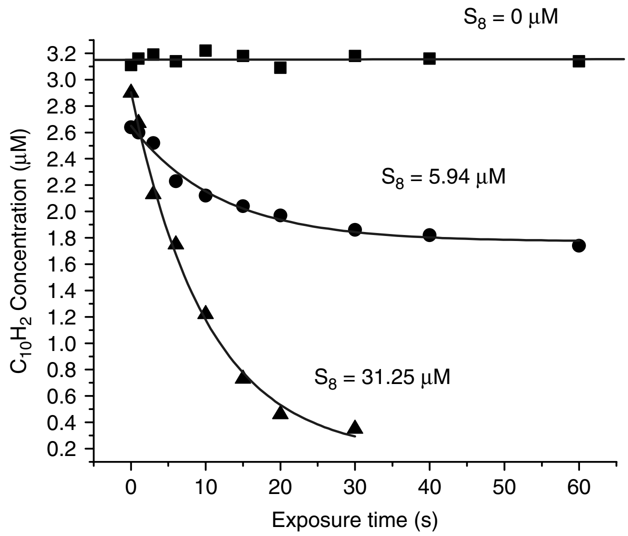


Fig. 2. Photolysis of $C_{10}H_2$ in n-hexane with the lamp immersed in the solutions. The c-S_8 concentrations shown are those at the start of the irradiation.

at 253.6 nm. Table 1 summarizes the results. Major contributions to uncertainties of Φ-values arise from the calibration of the photon flux (±10 %), the manual shuttering (±10 %), HPLC peak area determinations (±3 %) and of the ε_6 and ε_8 determinations (±3 %). The compounded uncertainty of the data in Table 1 could well be in the range of 20–40 %.

Exploratory photolysis of $C_{10}H_2$ without and with c-S_8 present was performed with the ultraviolet lamp actually immersed in the solutions contained in an air-cooled Pyrex tube. Short exposures times were measured from immersion to removal of the lamp. The results are shown in Figure 2. More than 90 % of the c-S_8 initially present was converted mostly to c-S_6 and c-S_7 after only 30 s of exposure. The exploratory runs were kept short for that reason. The following three observations can be made.

1. The rate of $C_{10}H_2$ photolysis without c-S_8 present was real but slow, which is a confirmation of earlier work by Cataldo (2004). To test whether the photolysis of $C_{10}H_2$ with 253.6-nm radiation might have been impeded by O_2 quenching, an identical experiment was performed after thorough purging of the solution with dry N_2. No detectable difference was observed.
2. When c-S_8 was present, $C_{10}H_2$ was transformed into one or several compounds whose composition could not be ascertained (see below).
3. The initial rate of transformation of $C_{10}H_2$ was proportional to the initial c-S_8 concentration.

For subsequent experiments the lamp was placed outside the cuvette that contained the solutions. A solution of 1.36 μM of $C_{10}H_2$ without sulphur was exposed for a total of 14 min. Samples were taken and analysed after 2, 6 and 14 min. The initial conversion rate of $C_{10}H_2$ in 1 cm^3 volume was -2.7×10^{-13} μM s^{-1}. Equation (1) was used with R_0, the initial destruction rate of $C_{10}H_2$, and A_0, the fraction of 253.6-nm photons absorbed by $C_{10}H_2$. Φ was 3×10^{-5}. An analogous experiment with a solution initially containing 0.885 μM $C_{10}H_2$ and 31.25 μM c-S_8 yielded an initial $C_{10}H_2$ conversion rate of -3×10^{-11} μM s^{-1}, two orders of magnitude faster than the transformation rate without sulphur present. The absorption of photons by c-S_8 did not require corrections for A_0. Φ was 7×10^{-3}.

As $C_{10}H_2$ absorbed at least 50 % of all 253.6-nm photons that entered the solutions in all experiments with sulphur present, the question arose of whether the observed faster transformation in the presence of sulphur implied that the polyyne molecules themselves had to be in an electronically excited state. To examine this, analogous experiments were carried out with C_8H_2, also obtained by the immersed carbon-arc method, whose solutions in n-hexane were essentially 100 % transparent at 253.6 nm (the strongest C_8H_2 absorption band in n-hexane above 200 nm is at 227 nm). In the presence of sulphur, C_8H_2 was transformed to unidentified product(s) with a rate similar to that of $C_{10}H_2$. Obviously, the reaction of C_8H_2 occurred with that molecule in the ground state. By inference it is suggested that the reaction of $C_{10}H_2$ with sulphur also occurred with that reactant in the ground state.

A search was made in all HPLC chromatograms for peaks due to products of putative reactions of $C_{10}H_2$ with sulphur. None were detected, perhaps because their molar extinction coefficients were too small, because their retention times were too long or because many different products were formed each with an undetectably small concentration. Nothing significant could be gained by increasing the $C_{10}H_2$ concentration because of its large molar extinction coefficient. Successful searches for products will require much more powerful ultraviolet sources.

Strauss and Steudel (1987) argued that ultraviolet radiation 'opens' the c-S_8, c-S_7 and c-S_6 rings to produce 'linear' diradical intermediaries, which then form S_n polymers as well as several other S_n molecules. The hypothesis of 'ring opening' is accepted here.

The most salient observations of the sulphur photolyses are as follows.

1. The Φ values are in the range 0.2–0.7 (Table 1), which implies that the 253.6-nm photons are very efficient in opening c-S_8 and c-S_6 rings.
2. The Φ values are independent of concentration, hence the ring openings are first-order processes.
3. The sum of the Φ values of the primary products from c-S_8 and c-S_6 appear to be roughly equal to the Φ value of the intermediary, which implies that little, if any, photopolymer is formed.
4. The number of atoms of c-S_6 and c-S_7 formed is roughly equal.

When only traces of photopolymer are formed, the most likely initial reactions of the photolysis of c-S_8 are

$$\text{c-}S_8 + h\nu \rightarrow \text{o-}S_8{}^* \rightarrow \text{c-}S_6 + S_2 \qquad (2)$$

$$\text{c-}S_8 + h\nu \rightarrow \text{o-}S_8{}^* \rightarrow \text{c-}S_7 + S \qquad (3)$$

$$\text{c-}S_8 + h\nu \rightarrow \text{o-}S_8{}^* + M \rightarrow \text{c-}S_8 + M^* \qquad (4)$$

However, one may expect the rate of polymer formation, which is at least a bimolecular process, to increase for higher initial concentrations of c-S_8 than those used in this study.

Theoretical calculations (Millefiori & Alparone 2001) show that reactions (2) and (3) each consume more than 100 kJ mol^{-1} of energy. To obtain a theoretical energy of the c-S_8 'ring opening', the total energies of the c-S_8 ring in the singlet ground state and of the o-S_8 biradical in the triplet ground state were calculated here with the B3LYP method and the 6-311G* basis set (Spartan '04 program; Wavefunction Inc., Irving, California, USA). The equilibrium configuration of the o-S_8 biradical turns out *not* to be linear but 'kinked' and the molecule has an electric dipole moment of 0.78 Debye. The ring opening requires 143.7 kJ mol^{-1}. The energy of a 253.6-nm photon is 417.7 kJ mol^{-1}. The biradical obviously has enough internal energy for additional S–S bond ruptures to eventually yield c-$S_6 + S_2$ and c-S_7+S through channels of essentially equal and surprisingly large transmission factors.

Strauss and Steudel (1987) did not attempt to prove that S and S_2 were actually formed in solution by photolysis of c-S_8. These sulphur species can be detected by chemoluminescence (Richter *et al.* 1998) and fluorescence (Grim & Greenberg 1987), but only at very low temperatures. In the course of the present study the smell of H_2S was detected above freshly photolysed solutions of c-S_8 in n-hexane and methanol. The formation of that compound was confirmed by the precipitation of PbS in a solution of lead nitrate in water into which the evolved H_2S gas was absorbed. Although the formation of H_2S is not absolute proof that the photolysis of c-S_8 produced S and/or S_2, the abstraction by these species of hydrogen from n-hexane, methanol or dissolved water is the most compelling explanation for the H_2S formation. S, S_2, o-S_8 and other biradicals are arguably the most reactive sulphur species in solution of c-S_8 photolysis.

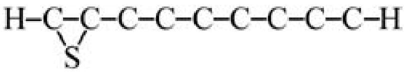


Fig. 3. A hypothetical product of the reaction of S with $C_{10}H_2$.

The energy of a 253.6-nm photon is also ample to open the c-S_6 ring whose bond energy per sulphur atom is actually 0.06 eV *less* than that of c-S_8 (Millefiori & Alparone 2001). However, c-S_6 has *fewer* sulphur atoms than both of its major products c-S_7 and c-S_8, hence its photolysis cannot be accounted for by a set of three dissociations analogous to those for c-S_8. Perhaps this photolytic process produces copious numbers of S, S_2, S_3, S_4 and c-S_5 species, which, in turn, react with mainly c-S_6 or o-S_6 to form the products. Once again it is remarkable that these processes are so efficient in the dilute solutions of this study. The photolysis of c-S_7 produces c-S_6 and c-S_8 (Strauss & Steudel 1987). c-S_6 might simply form by c-S_7+hν→o-$S_7{}^*$→c-S_6+S, but the formation of c-S_8 requires a formal scheme of c-S_7+S→c-S_8. It is revealing that the major products of the photolysis of c-S_8 are *not* c-S_7 and c-S_9 but c-S_6 and c-S_7. Apparently, the dissociations of the excited o-$S_8{}^*$ to c-S_6 and c-S_7 overwhelm processing through all other possible channels.

The data obtained strongly suggest that $C_{10}H_2$ reacts with some sulphur species when exposed to 253.6-nm radiation. A firm assignment of such species is still somewhat speculative because the sulphur-bearing products could not be identified. Nevertheless, it seems reasonable to assume that $C_{10}H_2$ reacted with the most chemically active photolytic sulphur species S and S_2, which suggests that facile photolytic reaction may occur with the astronomically abundant molecules H_2S, CS_2 or COS, which are known to produce S by ultraviolet photolysis. Some astrochemical consequences have been discussed elsewhere (Cataldo 2000; Cataldo & Heymann 2001; Heymann *et al.* 2000).

The simplest imaginable scheme is the reaction of S with $C_{10}H_2$ forming an HCSC ring on the polyyne molecule as shown in Figure 3. Dr. N.M.M. Nibbering (Private communication, 2006) suggested a scheme beginning with the attachment of an S atom at C-atoms 2, 3 and an S atom at C-atoms 8, 9 of $C_{10}H_2$ that following C—C cleavage of the three-member S-containing rings would give HCCSCC-CCCCSCCH. The latter molecule might then undergo four ring closures and one ring cleavage to eventually form a central benzene ring with two dehydrothiophene rings attached. $C_{10}S_2H_2$, C_4H_2 and C_6H_2, the polyynes that have actually been detected in astronomical environments, are more likely to yield dehydrothiophene-type molecules.

Cysteine and methionine were mentioned in the introduction as examples of basic constituents of biochemistry. Both have odd numbers of carbon atoms whereas $C_{10}H_2$ obviously has an even number. The salient point, however, is that possibly many carbon molecules with triple or even double C—C bonds, including molecules with odd numbers of carbon atoms such as the carbenes C_3H_2, C_5H_2, C_7H_2 and C_9H_2, all four surprisingly abundant interstellar molecules (Thaddeus *et al.* 1998), may react with photolytically produced S and/or S_2 to produce precursors of organic sulphur-bearing molecules.

COS, CS, H_2S and C_3S are identified interstellar molecules (Irvine *et al.* 1991). Diacetylene and triacetylene were discovered in the proto-planetary nebula CRL 618 (Cernicharo *et al.* 2001). Hence, circumstellar and interstellar media with ample ultraviolet radiation might well be favourable 'breeding grounds' for biochemically interesting S-bearing organic molecules. The Solar-System satellites Titan and Io are intriguing in this respect. The atmosphere of the former clearly contains C_2H_2, C_4H_2 and C_6H_2, but the molecular forms in which the element sulphur occurs are less clear. The atmosphere of the latter is periodically rich in S and S_2 due to volcanic outbursts, but polyynes are not known to occur. Polyynes and sulphur are known to occur in the atmosphere of Jupiter, but ultraviolet photolysis can only happen in the very outer reaches owing to the high density of the Jovian atmosphere.

Note added in proof: Continuing study of the polyyne suggests that its photolysis is strongly quenched by dissolved oxygen gas.

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