Matrix Isolated 1,2-Oxathietan-4-one 2-Oxide: a $2\pi + 2\pi$ Adduct of Sulphur Dioxide and Keten

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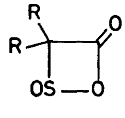
Summary U.v. irradiation of mixtures of SO_2 and keten in argon or nitrogen matrices at 10—20 K gave an adduct, identified on the basis of its i.r. spectrum and photodecomposition to carbon dioxide, as 1,2-oxathietan-4-one 2-oxide (5).

CYCLOADDITION reactions involving sulphur dioxide have been known for over 60 years and continue to elicit the interest of both experimental and theoretical chemists.[1] In nearly all the reactions studied, SO_2 adds in a 4 + 2 mode, and reports of 2+2 cycloadditions of SO_2 have remained rare. Unstable 2+2 adducts have been proposed



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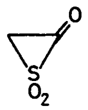

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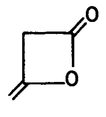

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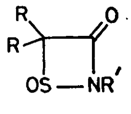
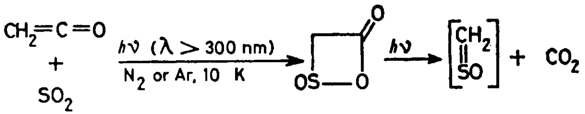


(4)

to account for the observed products in the photoreaction of SO_2 with certain fluoroalkenes,[2] and thermal reactions between ketens and SO_2 have also been rationalized on a similar basis, the unstable intermediates being assigned either the oxathietanone structure (**1**) (R = Ph or R_2 = $-[CH_2]_5-$)[3] or, in the case of keten itself, the three-membered ring structure (**2**).[4]

We now report the observation, in inert matrices at 10—20 K, of a photoadduct of SO_2 and keten, to which we assign the oxathietanone structure (**5**).



(5) **(6)**

When a gas mixture of keten, sulphur dioxide, and nitrogen (ratio 1 : 20 : 250) was condensed on a cold window at 20 K, the resulting matrix had an i.r. spectrum consisting solely of bands due to keten[5] and SO_2.[6] There was no evidence for the formation of a thermal adduct under these conditions. Upon u.v. irradiation of the sample (125 W Hg-arc, λ>300 nm and water-filter), the i.r. bands due to keten decreased in intensity and new bands arose. Of particular interest was a pair of bands at 1856 and 1840 cm^{-1}, in the region of the spectrum characteristic of the $\nu_{C=O}$ absorptions of β-lactones[7] [Figure (a)]. At this stage, only a small amount of CO_2 (i.r. bands at 2349 and 660 cm^{-1}) was present in the matrix. On further photolysis (Hg-arc, water-filter only), the bands at 1856 and 1840 cm^{-1} diminished in intensity while the CO_2 bands grew [Figures (a) and (b)]. On prolonged irradiation the bands at 1856 and 1840 cm^{-1} completely disappeared. I.r. bands at 1805, 1495, 1183, 906, 744, and 571 cm^{-1} (and several other weaker bands) increased and diminished in the same way as the bands at 1856 and 1840 cm^{-1}, and can therefore probably be attributed to the same species. Very similar changes in the i.r. spectrum were also observed in argon as well as nitrogen matrices.

The bands at 1856 and 1840 cm^{-1} did not arise when matrices containing either SO_2 or keten alone were irradiated, and they cannot be attributed to the dimer (**3**) of keten, which in an N_2 matrix at 10 K (ratio 1 : 250), had i.r. bands at 1905, 1873, and 1880 cm^{-1} and reverted to keten on photolysis (Hg-arc, water-filter), with no apparent formation of CO_2.

On the basis of the i.r. spectrum and ultimate generation of CO_2, we propose that the matrix photoreaction of SO_2 and keten proceeds by $2\pi + 2\pi$ cycloaddition to give 1,2-oxathietan-4-one 2-oxide (**5**).

The subsequent photodecomposition of (**5**) should produce sulphine (**6**) as well as CO_2, but we have so far been unable to detect sulphine (gas phase i.r. bands[8] at 1170 and 760 cm^{-1}) at any stage of the photolysis. This may be due to low intensity of the sulphine i.r. bands compared with those of CO_2, but most probably, sulphine is decomposed photochemically as rapidly as it is formed.

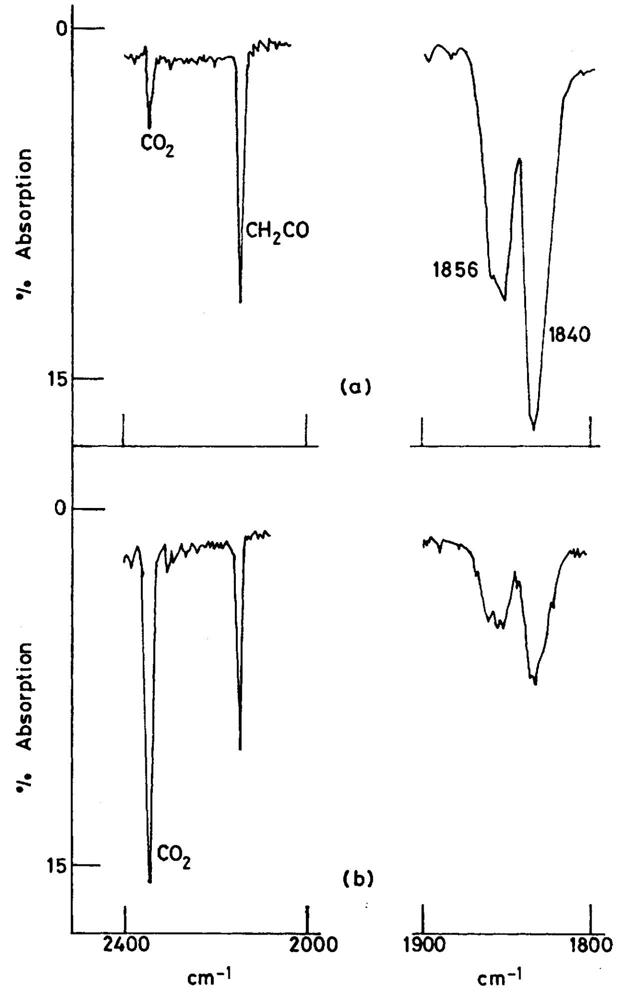


FIGURE. (a) I.r. spectrum of CH_2CO and SO_2 in N_2 (1 : 20 : 250) at 10 K, after 645 min irradiation (Hg-arc, λ>300 nm, water-filter). (b) After further 475 min irradiation (Hg-arc, water-filter only). Matrices were prepared by the pulsed matrix isolation method and i.r. spectra were recorded on a JASCO IRA-2 spectrophotometer.

The i.r. spectrum of a 1,2-oxathietan-4-one 2-oxide has not previously been reported. The $\nu_{C=O}$ bands of (**5**) are close to those of β-lactones[7] (*e.g.* the parent compound, propiolactone, has bands at 1866 cm^{-1} in the gas phase and 1831 cm^{-1} in solution), and this suggests that the sulphoxide group has little effect upon the $\nu_{C=O}$ frequency, or at most reduces it by 20—30 cm^{-1}. A similar observation has been made with β-lactams. These typically have $\nu_{C=O}$ bands[9] in the range 1790—1770 cm^{-1}, whereas the thiazetidinone *S*-oxides of general structure (**4**) have bands at 1760—1730 cm^{-1}, again showing only a slight negative shift in the $\nu_{C=O}$ frequency due to the ring sulphoxide.[10]

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