Photochemical 2 + 2-Cycloadditions of Sulphur Dioxide and Ketenes in Low-temperature Matrices

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U.v. irradiation at 12 K of Ar or N_2 matrices containing ketenes and SO_2 yielded the corresponding 1,2-oxathietan-4-one 2-oxides as 2 + 2-cycloadducts; this reaction was shown to be distinct from the thermal 1 + 2-cycloaddition of ketene and SO_2. The 2 + 2-adducts decomposed on prolonged irradiation to CO_2, sulphur atoms, and the corresponding aldehydes or ketones, presumably *via* sulphines, which, however, could not be detected. Interpretation of the spectra was complicated by strong interactions between carbonyl compounds and SO_2, and this phenomenon was also explored.

As long ago as 1912, Staudinger reported the discovery of a thermal adduct from sulphur dioxide and ketene, and assigned to it the oxathietanone structure (**1**; $R^1 = R^2 = H$).[1] Some 60 years later, analogous adducts from substituted ketenes were described, and these were also assigned oxathietanone structures (**1**; $R^1 = R^2 = Ph$ or $R^1,R^2 = [CH_2]_5$).[2] Joullié and her co-workers, however, subsequently provided ^1H n.m.r. evidence that the thermal reaction between SO_2 and ketene gives, not the 2 + 2-cycloadduct (**1**; $R^1 = R^2 = H$), but the 1 + 2-adduct (**2**).[3]

As might be expected, the photochemical reaction follows a different pathway. Recently, we reported our preliminary findings on the u.v.-induced reaction between SO_2 and ketene isolated in inert matrices at 12 K.[4] The results suggested that the initial product in these conditions was the oxathietanone (**1**; $R^1 = R^2 = H$) originally proposed as the thermal adduct. We now describe further matrix studies which support our earlier conclusion and extend the reaction to other ketenes.

Experimental

Equipment.—The matrix isolation cold cell was similar to that described by Turner and his co-workers.[5] It consisted of a CsBr window and a nickel-plated copper holder in thermal contact with the cold end of an Air Products Displex, model CSA-202, closed-cycle helium refrigerator. The cold window was enclosed in a glass and metal vacuum shroud fitted with external KBr windows and one or two inlet ports for sample deposition. The shroud was pumped to 10^{-6}—10^{-7} Torr by means of an Edwards Diffstak model 63-150M oil diffusion pump. Temperature measurements of the cold end of the cell were made by means of (i) a hydrogen vapour bulb and (ii) a Chromel–Au–0.07 atom-% Fe thermocouple connected to an Air Products, model APD-B temperature controller. The base temperature of the cell was 12 K, and temperatures above this were achieved by means of a small resistance heater connected to the temperature controller and placed in thermal contact with the cold end of the cell. A small secondary vacuum line, used for handling the matrix gases and controlling deposition rates, was connected to the shroud *via* a fine control needle-valve. The whole matrix system was mounted on an overhead gantry from which the cold cell was suspended. This arrangement allowed movement of the cell from one spectrometer to another and also to convenient locations for u.v. irradiation.

A simple preparative vacuum line was used for making up matrix gas mixtures by conventional manometric techniques.

I.r. spectra, in the range 4 000—400 cm^{-1}, were recorded on an unmodified JASCO model IRA-2 spectrometer. Spectra were calibrated against polystyrene film, and frequencies quoted are accurate to ± 4 cm^{-1} (above 2 000 cm^{-1}) or ± 2 cm^{-1} (below 2 000 cm^{-1}). U.v.–visible spectra were recorded on a Pye-Unicam model SP1800B spectrometer, with a modified sample compartment able to accommodate the cold cell.

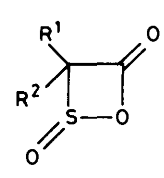
U.v. irradiation was achieved by means of a Philips HPK 125W medium-pressure Hg arc. A water-cooled water filter (13 cm path-length) with quartz windows was placed in the beam at all times, in order to remove i.r. radiation. Soda-glass ($\lambda > 330$ nm) and Pyrex ($\lambda > 300$ nm) cut-off filters were also used occasionally. The lamp was mounted on a small trolley, and both sides of the matrix could be irradiated.

In addition to the main matrix isolation unit, a simple liquid nitrogen-cooled cryostat was also constructed. It consisted of a KBr window and copper holder, attached by means of a graded seal to the bottom end of a Pyrex liquid nitrogen vessel. This combination was enclosed, at the lower end, in a glass vacuum shroud fitted with external KBr windows, an outlet port for pumping, and an inlet port for sample deposition. No means of temperature control or measurement were fitted to this cell.

Matrix Gases.—Research grade N_2 ($\nless 99.994\%$), Ar ($\nless 99.9997\%$), and CO ($\nless 99.96\%$) were obtained from B.O.C. Ltd. and were used without further purification. Sulphur dioxide was obtained from B.D.H. Ltd., and was purified by vacuum transfer from low-temperature traps. The sample of 70 atom-% ^{18}O-enriched sulphur dioxide was obtained from B.O.C. Prochem. Ltd., and was used without further purification.

Compounds.—Ketene was prepared by passing acetone in a stream of N_2 through a quartz tube at 780 °C, followed by trapping at 137 K.[6] The crude ketene was purified by vacuum distillation at 185 K and degassing at 77 K, and the purified material was stored under vacuum at 77 K. Diphenylketene was prepared by thermolysis of diazophenylbenzoylmethane,[7] and was stored under vacuum at −10 °C. Methylketene was prepared by pyrolysis of propionic anhydride at 600 °C,[8] and was stored under vacuum at 77 K. Phenylethylketene was prepared by treating α-phenylbutyryl chloride with Et_3N in hexane at room temperature,[9] and was stored under vacuum at −10 °C.

Formaldehyde was prepared by thermolysis of paraformaldehyde,[10] and was stored under vacuum at 77 K. Carbon suboxide was prepared by dehydration of malonic acid,[11] and was stored under vacuum at 77 K. All other carbonyl compounds were commercial samples, further purified by vacuum distillation or sublimation.



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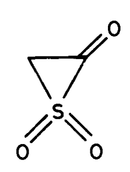

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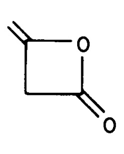

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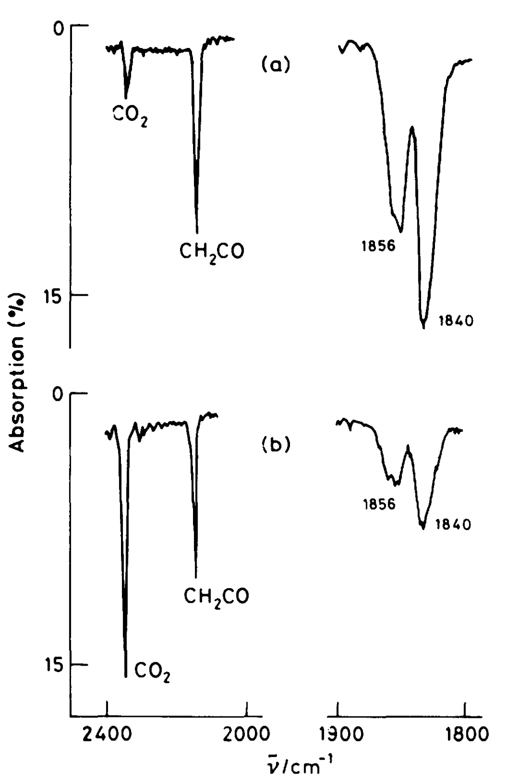


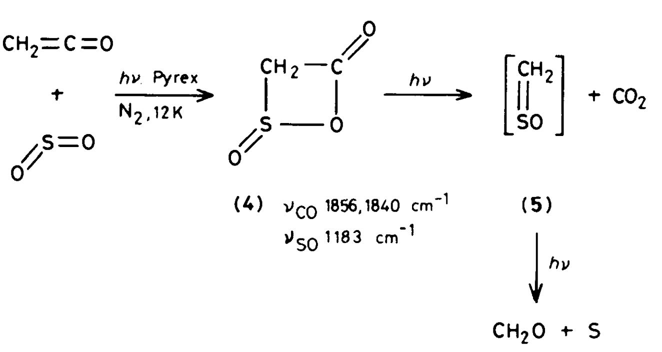
Figure 1. I.r. spectra recorded after irradiation of CH_2CO and SO_2 in N_2 (1:20:250) at 12 K. (a) After 645 min (λ >300 nm); (b) after a further 475 min (λ > 200 nm)

4-Methyl-1,2,3-selenadiazole was prepared by the action of selenium dioxide on acetone semicarbazone.[12]

Matrix Deposition.—Compounds with high enough vapour pressures at room temperature (0.5 Torr or more) were mixed with the appropriate matrix host gas on the preparative vacuum line. The matrix ratios (MR) were determined manometrically. The resulting gas mixtures were then allowed to condense on the cold window at 20 K, either at a controlled rate through the needle valve, or in small (2—10 cm^3) pulses.[13] The matrices were usually cooled to 12 K before photolysis or spectroscopic examination. Less volatile compounds were sublimed directly onto the cold window from a sample tube connected to the vacuum shroud, while the matrix host gas was allowed to condense simultaneously at a controlled rate. In these circumstances, matrix ratios could not be estimated.

Results and Discussion

Ketene and SO_2.—When a gas mixture of ketene, 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 ketene[14] and SO_2.[15] There was no evidence for the formation of a thermal adduct under these conditions. Upon u.v. irradiation of the matrix (λ > 300 nm), at 12 K, the i.r. bands of ketene decreased in intensity and new bands arose. Of particular interest was a pair of bands at 1 856 and 1 840 cm^{-1}, in the region of the spectrum characteristic of β-lactones[16] [Figure 1(a)]. At this stage, only a small amount of CO_2 (i.r. bands at 2 349 and 660 cm^{-1}) was present in the matrix. On further photolysis (water-filter only), however, the bands at 1 856 and 1 840 cm^{-1} diminished in intensity while the CO_2 bands grew [Figure 1(b)]. On prolonged irradiation the bands at 1 856 and 1 840 cm^{-1} completely disappeared. I.r. bands at 2 964, 1 805, 1 183, 906, 882, 744, 630, 571, and 472 cm^{-1} increased and diminished along with the bands at 1 856 and 1 840 cm^{-1}, and are therefore attributed to the same species. Very similar results were also observed for argon matrices.



Scheme 1.

The bands at 1 856 and 1 840 cm^{-1} did not arise when matrices containing either SO_2 or ketene alone were irradiated, nor can they be attributed to the dimer (3) of ketene, which at 12 K in an N_2 matrix containing SO_2 [MR (3):SO_2:N_2, 1:20:250] had i.r. bands at 1 888, 1 861, and 1 695 cm^{-1}, and reverted to ketene on photolysis (Hg arc; water filter only), with no apparent formation of CO_2. The species formed from ketene and SO_2 was therefore most probably an adduct of the two molecules.

The photochemical adduct of ketene and SO_2 was shown to be distinct from the thermal adduct by experiments at 77 K using the liquid-nitrogen cryostat. When a gas mixture of ketene and SO_2 (ratio 1:40) was condensed on a KBr window at 77 K, the resulting sample had an i.r. spectrum which had bands at 1 828 and 1 800 cm^{-1} in addition to those belonging to the two reactants. On annealing the sample, these additional bands grew in intensity, and are therefore attributed to the thermal adduct, thiiranone 1,1-dioxide (2), following Joullié's assignment.[3] When the experiment was repeated and the sample was irradiated (λ > 300 nm) rather than annealed, new i.r. bands at 1 840 and 1 820 cm^{-1} grew in alongside those belonging to (2). The bands belonging to (2) did not change in intensity during the photolysis. We assign the bands at 1 840 and 1 820 cm^{-1} to the same photoadduct observed in N_2 matrices at 12 K, attributing the 16—20 cm^{-1} difference in frequencies to a solvent shift (see below).

The course of the matrix photochemistry is best accounted for on the supposition that the initial photoadduct of ketene and SO_2 is the 2 + 2-cycloadduct (4), which subsequently decomposes to CO_2 and presumably sulphine (5) (Scheme 1). We have not been able to detect sulphine at any stage in our experiments, however. This is not surprising, because sulphines are known to decompose photochemically to the corresponding carbonyl compounds and sulphur atoms.[17] Thus in the matrix photodecomposition of (4), the observed ultimate products are formaldehyde and sulphur atoms. The latter do not, of course, give rise to an i.r. absorption, but are detectable by the

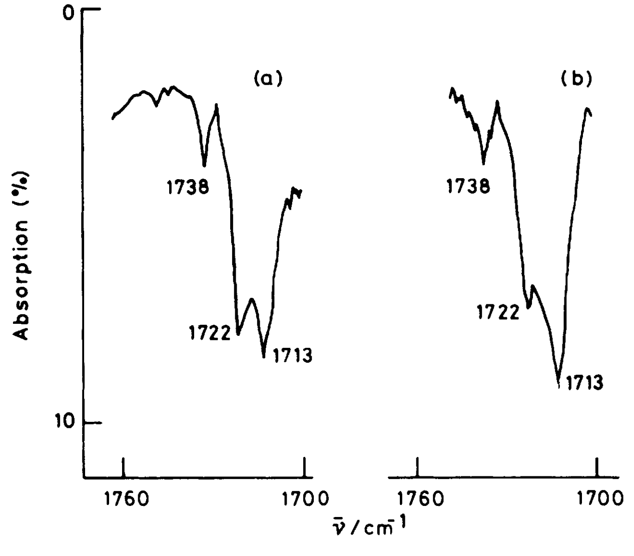
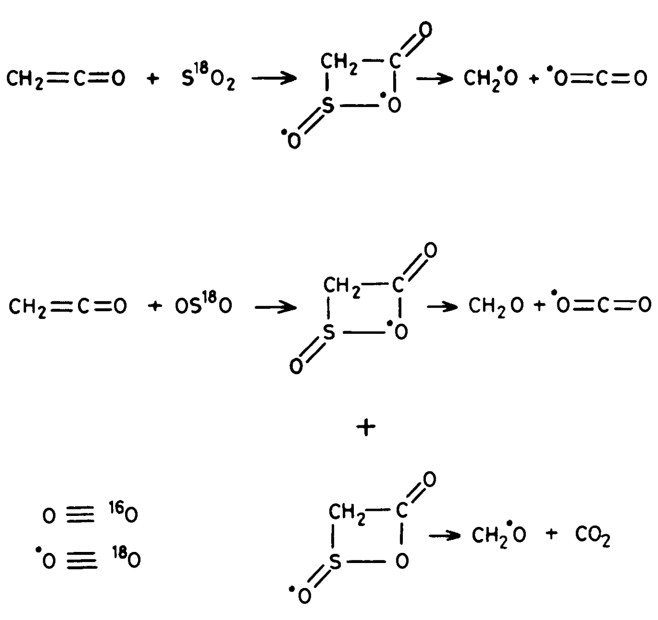


Figure 2. Carbonyl bands of CH_2O in the presence in SO_2 in N_2 matrices at 12 K. (a) CH_2O generated by photolysis of CH_2CO and SO_2 in N_2 (1 : 20 : 250); (b) authentic CH_2O and SO_2 in N_2 (1 : 12 : 100)

characteristic blue chemiluminescence resulting from atom recombination,[18] which was always observed when the matrices were warmed at the end of the experiments. The formaldehyde produced gave rise to an i.r. spectrum which, with the exception of one band, agreed closely with previous results for this molecule (bands at 2 856, 2 812, 1 713, 1 522, 1 500, and 1 241 cm^{-1}). The exception was the $\nu_{C=O}$ band at 1 713 cm^{-1}, which was perturbed by SO_2 from its value of 1 741 cm^{-1} in pure N_2 matrices.[19] Matrices containing authentic formaldehyde and SO_2 reproduced this perturbation of the spectrum rather closely (Figure 2), and the interaction between carbonyl groups and SO_2 has since been found to be a general phenomenon (see Appendix). Thus in Scheme 1, only sulphine (**5**) remains undetected.

One further test of Scheme 1 could be made using ^{18}O-labelled SO_2. The reaction scheme is elaborated for the reactions of $S^{18}O_2$ and $S^{16}O^{18}O$ in Scheme 2. From this, the reader can readily see that for a 1 : 1 mixture of $S^{18}O_2$ and $S^{16}O^{18}O$, the expected products would be $C^{16}O_2$ and $C^{16}O^{18}O$ in the ratio of 1 : 3 (with no $C^{18}O_2$), and $CH_2{}^{16}O$ and $CH_2{}^{18}O$ also in the ratio 1 : 3. In practice we used labelled SO_2 containing 6.7% $S^{16}O_2$, 42.9% $S^{16}O^{18}O$, and 50.4% $S^{18}O_2$ (measured by cutting and weighing i.r. bands in the N_2-matrix spectrum of the labelled SO_2). Part of an i.r. spectrum obtained during the photolysis of an N_2 matrix containing ketene and labelled SO_2 (MR ketene : SO_2 : N_2, 1 : 2 : 100) is shown in Figure 3. The isotope bands of the products CO_2 and CH_2O are well resolved, although those of the intermediate (**4**) are not. Experimental band areas, estimated by cutting and weighing, are compared with the predicted areas in Table 1, and the two sets of values agree within experimental error. Thus, the distribution of ^{18}O in the products is completely consistent with the proposed reaction scheme.*

Substituted Ketenes and SO_2.—The 2 + 2-cycloaddition of SO_2 and ketene is not confined to ketene alone, but occurs also with diphenylketene, methylketene, and phenylethylketene, and is probably general for substituted ketenes. Irradiation (λ > 300 nm) of a N_2 matrix containing diphenylketene ($Ph_2C=C=O$) and SO_2 (MR 1 : 30 : 250) resulted in formation of an intermediate with i.r. absorptions at 1 843 and 1 828 cm^{-1}, and to which we assign the oxathietanone structure (**1**; $R^1 = R^2 =$ Ph). On prolonged irradiation (λ > 200 nm), this intermediate decomposed to benzophenone (Ph_2CO), CO_2, and sulphur atoms. As with formaldehyde, the benzophenone exhibited a $\nu_{C=O}$ band which was strongly perturbed by SO_2,



Scheme 2.

Table 1. Predicted and experimental relative areas for the ν_{CO} bands of the ultimate photoproducts in Scheme 2

Product	$\nu_{max.}/cm^{-1}$	Predicted area (%)[a]	Experimental area (%)[b]
$C^{16}O_2$	2 348	71.8	70.4
$C^{16}O^{18}O$	2 330	28.2	29.6
$C^{18}O_2$	2 311	0	*c*
$CH_2{}^{16}O$	1 720, 1 713	71.8	70.6
$CH_2{}^{18}O$	1 688	28.2	29.3

[a] Based on an initial isotope composition of $S^{16}O_2$:$S^{16}O^{18}O$:$S^{18}O_2$, 6.7 : 42.9 : 50.4. [b] Measured by cutting out bands as accurately as possible and weighing. [c] Not observed above noise level: expected band position from ref. 27.

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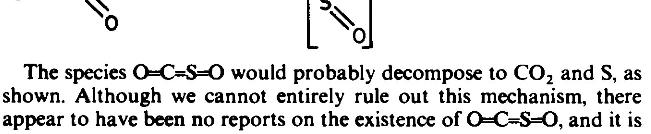
* We are grateful to a referee for promoting a discussion of the regiochemistry of the addition of SO_2 to ketene. Formation of the regioisomer of (**4**) would also be consistent with our observations provided that its photodecomposition proceeded as follows:



The species O=C=S=O would probably decompose to CO_2 and S, as shown. Although we cannot entirely rule out this mechanism, there appear to have been no reports on the existence of O=C=S=O, and it is therefore likely to be a very unstable molecule. In view of the possible alternative photodecomposition back to SO_2 and ketene, we believe the photoextrusion of O=C=S=O would be very improbable. We therefore take the formation of CO_2 as an ultimate photoproduct to be evidence, though not conclusive evidence, in favour of structure (**4**) for the adduct of ketene and SO_2.

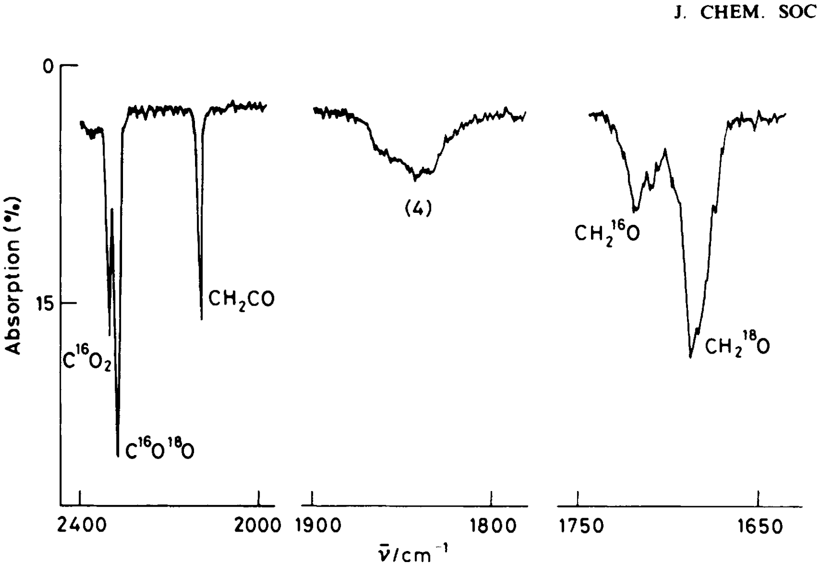
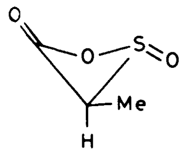


Figure 3. I.r. spectrum obtained after irradiation (250 min, λ >300 nm; and 205 min, λ >200 nm) of CH_2O and 70 atom-% ^{18}O-labelled SO_2 in N_2 (1:2:100) at 12 K



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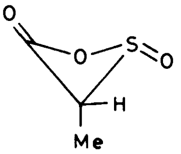

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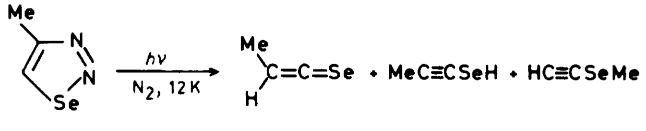

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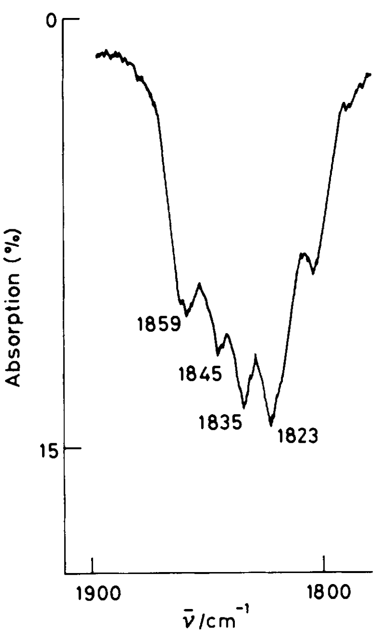

Figure 4. I.r. spectrum obtained after irradiation (λ >300 nm) of CH_3CHCO and SO_2 in N_2 (1:15:125) at 12 K

and the perturbed spectrum could be closely reproduced with N_2 matrices containing authentic benzophenone and SO_2.

Of more interest, perhaps, is the reaction between SO_2 and the unsymmetrically substituted ketene, methylketene (MeCH=C=O). With this starting material, unless the oxathietanone and its exocyclic oxygen are completely planar, the possibility of geometrical isomerism exists, in which the methyl group may be either *trans* (**6**) or *cis* (**7**) with respect to the sulphoxide oxygen. Irradiation (λ >300 nm) of a matrix of methylketene, SO_2, and N_2 (MR 1:15:125) produced a 2 + 2-cycloadduct whose i.r. spectrum is shown partially in Figure 4. The presence of four strong $\nu_{C=O}$ bands (1 859, 1 845, 1 835, and 1 823 cm^{-1}) and two $\nu_{S=O}$ bands (1 185 and 1 160 cm^{1}) clearly suggests the formation of two isomeric oxathietanones (**6**) and (**7**). On prolonged photolysis (λ >200 nm), the i.r. bands of the 2 + 2-cycloadducts decreased in intensity, while those of the CO_2 and acetaldehyde (perturbed by SO_2) grew.

Similar irradiation (λ >300 nm) of a matrix of phenylethylketene PhC(Et)=C=O, SO_2, and N_2 gave rise to a 2 + 2-cycloadduct whose i.r. spectrum showed two broad bands at 1 842 and 1 824 cm^{-1} and two $\nu_{S=O}$ bands at 1 180 and 1 172 cm^{-1}. Although in this case the carbonyl bands were not well resolved, the presence of two sulphoxide bands suggests the formation of two geometric isomers as with (**6**) and (**7**).

Ketene Analogues and SO_2.—In view of the apparent generality of the photocycloaddition of SO_2 and ketenes, we tried a number of other heterocumulenes as replacements for the ketene partner in this reaction. All these attempts, however, have proved unsuccessful. Thus phenyl isocyanate (PhN=C=O), methyl isocyanate (MeN=C=O), and carbon suboxide (O=C=C=C=O) were all readily incorporated into SO_2-doped matrices and all failed to given any photoadduct with SO_2. Irradiation (λ >300 nm) of a N_2 matrix containing 4-methyl-1,2,3-selenadiazole (**8**) gave a mixture of methylselenoketene (**9**) ($\nu_{C=C=Se}$ 1 734 cm^{-1}) and small amounts of alkynes, probably (**10**) and (**11**), as expected from previous reports.[20] When the experiment was repeated with SO_2 present in the matrix, no new i.r. bands that could be assigned to a cycloadduct of the selenoketene and SO_2 were observed.

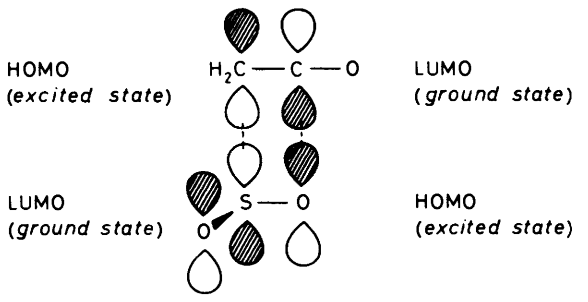

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Table 2. Observed ν_{CO} band intensities (% absorption) for N_2 matrices at 12 K containing CH_2O and varying proportions of SO_2[a]

Matrix ratio $CH_2O:SO_2:N_2$	Band maxima (cm^{-1}) 1 741	1 738	1 729	1 726	1 718	1 714
1: 0:1 000	46	27				
1: 1:1 000	33	27	22	*b*	6	
1: 10:1 000	21	*b*	21	*b*	12	
1: 40:1 000	22	*b*	*b*	35	*b*	22
1:100:1 000		7	*b*	22	*b*	37

[a] All the matrices were prepared by pulsing onto the window at 20 K 100 × 10 cm^3 volumes from a 1 l bulb originally containing 500 Torr of the gas mixture. The matrices were then annealed at 25 K for 5 min before cooling to 12 K. [b] Band obscured by overlap with neighbouring bands.

Conclusions.—Our results demonstrate that ketene and SO_2 can undergo either a photochemical 2 + 2-cycloaddition or a thermal 1 + 2-cycloaddition. Mechanistic considerations based on frontier orbital interactions commonly predict such divergence of thermal and photochemical pathways,[21] and may be appropriate here. Both ketene and SO_2 absorb only weakly in the u.v. above 200 nm, so that it is not yet clear which of the two reactants takes part in the photoaddition as the excited state. Despite this fact, the photoaddition may be comfortably fitted to a simple frontier orbital model, since the expected dominant interactions, HOMO (excited ketene)–LUMO (SO_2) or HOMO (excited SO_2)–LUMO (ketene), are both favourable (**12**).

Nevertheless, great restraint must be exercised in advancing any mechanistic hypothesis for these cycloadditions. First, there is no experimental evidence to support the postulate that either the thermal or the photochemical reaction is concerted. Indeed, there is every likelihood that the thermal 1 + 2-cycloaddition is a step-wise process, because for the closely related cycloreversion of episulphones, both experimental evidence and theoretical considerations concur in favouring a non-concerted or at least highly asynchronous cleavage of the C–S bonds.[22] Secondly, it is well known that ketene undergoes a wide variety of thermal 2 + 2-cycloadditions, some of which may be best rationalized as $\pi^2s + \pi^2a$-reactions,[23] but for which the possibility also exists for the operation of concerted $[\pi^2s + (\pi^2s + \pi^2s)]$ mechanisms such as have been proposed for allenes.[24] Finally, it has been pointed out, with respect to the cycloreversion of β-sultines, that strong asymmetrization of a concerted pathway, in particular by introduction of heteroatoms, can lead to reactions that are not well predicted by hydrocarbon-based symmetry rules.[25] In view of these complications, a rational choice of mechanism for the cycloadditions of ketene and SO_2 must await further understanding.

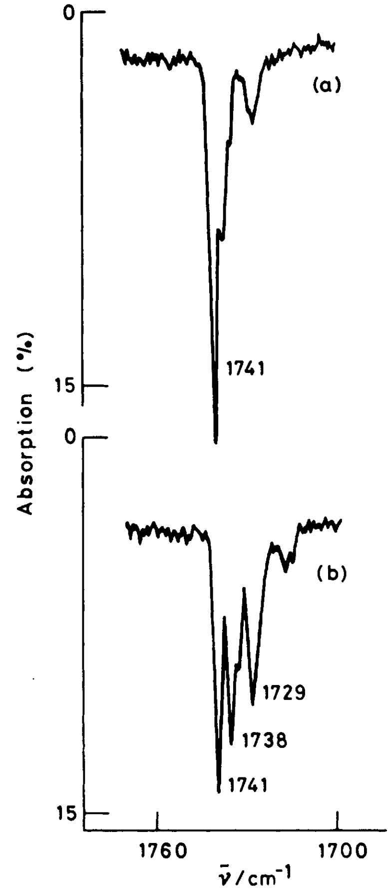

Figure 5. I.r. spectra of CH_2O and SO_2 in N_2 (1:1:500) at 12 K. (a) Before annealing; (b) after annealing for 2 min at 25 K and recooling to 12 K

Appendix

Interactions between SO_2 *and Carbonyl Compounds.*—During the course of this work, it became apparent that SO_2 molecules present in the matrix were capable of interacting strongly with the aldehydes and ketones liberated as ultimate photoproducts. This interaction resulted in substantial red-shifts of the ν_{CO} bands in the i.r. spectra of the carbonyl compounds, as illustrated for formaldehyde in Figure 2. Strong interactions of this type are to be expected between polar, particularly protic, or polarizable molecules in matrices.[26]

The precise nature of the SO_2–formaldehyde interaction was probed further by observation of (i) the effect of annealing matrices containing formaldehyde and SO_2 and (ii) the effect of varying the SO_2 concentration. Figure 5 shows the results of a typical annealing experiment, in which diffusion of the molecules at 25 K led to the growth of new carbonyl bands, all red-shifted from the unperturbed absorption. Table 2 summarizes the results of measurements of ν_{CO} band intensities for formaldehyde made with N_2 matrices containing varying amounts of SO_2. The general trend is very clear: as the concentration of SO_2 was increased, the intensities of the lower frequency bands increased, while those of the higher frequency bands decreased. The presence of several red-shifted ν_{CO} bands with differing concentration dependence argues against the formation of a CH_2O–SO_2 complex of precisely defined stoicheiometry and structure, and favours instead multiple trapping sites such that increasing numbers of neighbouring SO_2 molecules result in increasing perturbation of the formaldehyde C=O stretching mode.

Table 3. Observed ν_{CO} band positions for N_2-matrix-isolated carbonyl compounds at 12 K, in the absence and in the presence of SO_2[a]

Compound	ν_{CO} without SO_2/cm^{-1}	Lowest frequency ν_{CO} with SO_2/cm^{-1}	Maximum observed red-shift (cm^{-1})
Ph_2CO[b]	1 674	1 630	44
$(CH_3)_2CO$	1 723	1 686	37
CH_3CHO	1 739	1 709	30
CH_2O	1 741	1 713	28
CH_3CH_2CHO	1 744	1 695	49
$HCO_2CH_2CH_3$	1 738	1 696	42
$CH_3CO_2CH_3$	1 760	1 700	60
CH_2CO	2 142	2 142	0
CO_2	2 348	2 348	0

[a] Except for Ph_2CO, all matrices without SO_2 had matrix ratios of guest:N_2, 1:1 000, and all those with SO_2 had ratios of 1:1 000 in N_2 doped with 10% SO_2. [b] Matrices containing Ph_2CO was prepared by sublimation of the ketone and simultaneous deposition of pure N_2 or N_2 doped with 10% SO_2; in neither case could the ratio of Ph_2CO to host gas be determined.

In addition to the aldehydes and ketones arising from the reactions which form the main part of this work, we have studied the effect of SO_2 on a limited selection of other carbonyl compounds. Table 3 summarizes our results, from which it will be seen that esters also experience a pronounced interaction, whereas two molecules with high frequency carbonyl stretches (ketene and CO_2) do not. It is clear that all further work involving SO_2-doped matrices should be conducted with these quite strong interactions and the probability of other similar interactions firmly in mind.

To conclude the discussion of this topic, it is worth reconsidering the ν_{CO} bands in the spectra of oxathietanones (**1**). These all exhibited splitting reminiscent of that caused by SO_2 (*cf.* Figures 1 and 4). Nevertheless, the splitting in these bands has not shown the necessary dependence on SO_2 concentration or matrix host (N_2 or Ar), so that we are confident that the splitting is an intrinsic property of the matrix-isolated molecules and is not due to differing interactions with SO_2. On the other hand, these C=O stretches are undoubtedly sensitive to SO_2, as demonstrated by the red-shift observed for (**4**) on going from SO_2-doped N_2 matrices to the admittedly extreme case of solid SO_2. It can thus be assumed that the ν_{CO} bands reported for (**4**) and its analogues in this paper will be perturbed from the frequencies that would obtain in the absence of SO_2. It is likely that the perturbation is small since it has not been evident through many changes of conditions during our experiments, but its exact degree must remain a matter of conjecture for the time being.

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