Gas-phase Thermolysis of a Thioketen-*S*-Oxide [1,2]

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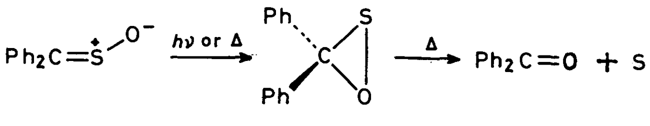
The unimolecular gas-phase thermolytic decomposition of 1,1,3,3-tetramethyl-2-thiocarbonylcyclohexane *S*-oxide (3) has been studied as a function of temperature by a flash vacuum thermolysis (f.v.t.) technique. The products detected are the carbenes (4) and (5), the ketone (6), the keten (7), the thioketone (8), and the thioketen (9). The product ratio is highly dependent on the thermolysis temperature. The thermolysis of (3) is mechanistically rationalized by assuming the existence of only two concurrent primary processes, which are (a) extrusion of atomic oxygen, leading to the thioketen (9), and (b) electrocyclic ring closure into the corresponding three-membered oxathiiran (10). The latter is dominant at lower temperatures, whereas higher thermolysis temperatures favour atomic oxygen extrusion. At further elevated temperatures additional concurrent primary reactions, *i.e.* extrusions of SO and CSO leading to the carbenes (5) and (4), respectively, are observed. Owing to an apparently very short half-life of the oxathiiran (10), only the decomposition products of the three-membered ring compound have been detected. These are the thioketone (8), formed by rearrangement of (10) into the α-thiololactone (11) followed by loss of CO, minor amounts of the ketone (6), formed analogously, and the keten (7), as a result of simple sulphur extrusion.

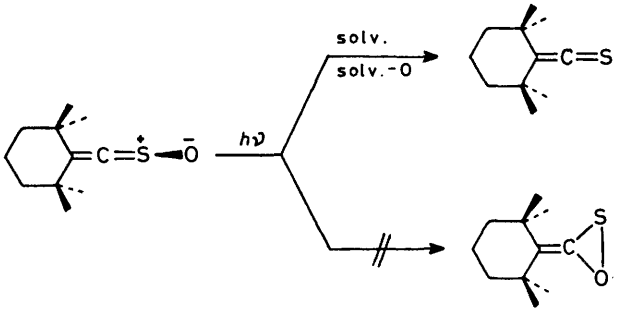
In connection with our continuing interest in the thermal and photolytical transformations of thiocarbonyl *S*-oxides (sulphines), we previously reported the electrocyclic ring closure of thiobenzophenone *S*-oxides (1) into



(1) (2)

the corresponding 3,3-diaryloxathiirans (2), as a thermally [3] as well as a photolytically [4-6] induced reaction. However, we found oxathiirans to be thermally highly labile compounds,[3-6] which at room temperature rapidly decompose into the corresponding ketones and elemental sulphur.

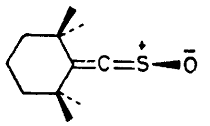
In contrast to this we found that thioketen *S*-oxides are deoxygenized photolytically, presumably by reaction between the excited thioketen *S*-oxide molecule and the solvent.[7] The resulting thioketen was detected in 95% yield together with only vanishingly small amounts (<3%) of the keten. On this basis we concluded that



the possible formation of a methyleneoxathiiran does not play any major role in the photolysis of thioketen *S*-oxides.

In this paper we report results on the gas-phase thermolysis of 1,1,3,3-tetramethyl-2-thiocarbonylcyclohexane *S*-oxide (3),[1,8] which at room temperature is a thermally stable thioketen *S*-oxide. We have investigated the thermal decomposition of (3) in an attempt to study possible ring closure to the methyleneoxathiiran and/or thioketen formation as a result of extrusion of atomic oxygen, analogous to the above mentioned photodeoxygenation.[7]

The thermolysis of (3) was studied by a flash vacuum thermolytic (f.v.t) procedure,[9] which secures detection of unimolecularly formed products alone and predominantly, only primary thermolysis products.



(3)

EXPERIMENTAL

The thioketen *S*-oxide (3) was prepared by peracid oxidation of the corresponding thioketen, as described previously.[8]

Flash Vacuum Thermolysis Technique.[9]—The f.v.t. technique is based on the direct combination of a thermolysis unit with a double focusing mass spectrometer with a field ion source. The thermolysis unit is constructed as a modification of the Pye-Unicam PV4000 pre-column-pyrolysis system, which is based on the Curie point principle, *i.e.* high frequency inductive heating in ferromagnetic materials. The thermolysis unit is connected directly to the ion source of the mass spectrometer *via* a heated line-of-sight inlet system.

Samples (*ca.* 50 μg) of the pure compound were introduced (microsyringe) into the reactor *via* a heated injection block. The contact time in the hot zone has been estimated to be *ca.* 10^{-3}—10^{-4} s,[9] fullfilling the contact time requirement for f.v.t. equipment.[10] Because of the geometry of the system thermolysis products with half-lives < *ca.* 10^{-3} s are assumed to escape detection.[9] The internal geometry of the reactor (*l* 40 mm, i.d. 2 mm) combined with the low pressure (*ca.* 10^{-4} Torr) assure a very low frequency of intermolecular collisions relative to the molecule-hot surface collision frequency, *i.e.* only unimolecular reactions take place.

The mass spectra were recorded on a Varian MAT CH 5D instrument (the magnetic sector preceeding the electric sector) equipped with a combined electron impact ionization–field ionization–field desorption ion source. The field ion emitter was a 10 μm tungsten wire activated in benzonitrile vapour. The maintenance of the vacuum in the system is based on differential pumping of the ion source, analyser tube, and the electric sector. Pumping speed was 3 × 150 l s^{-1}.

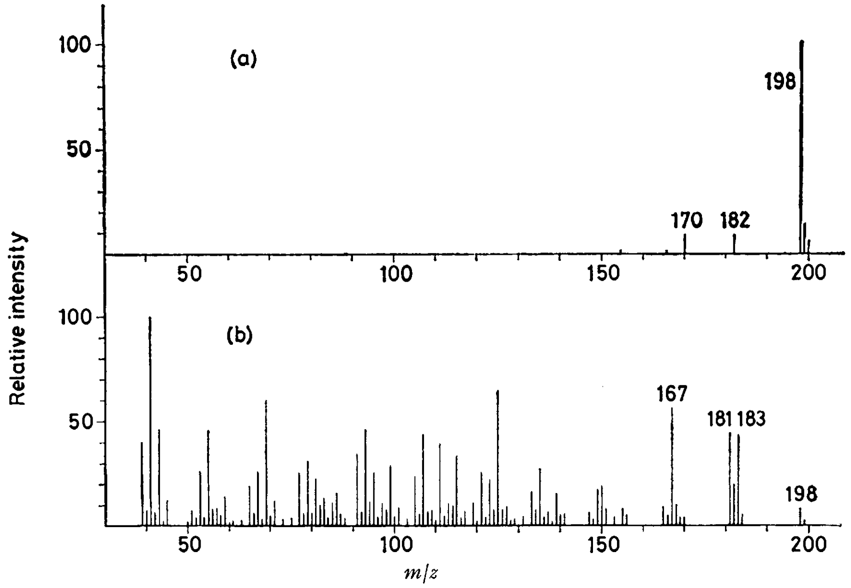


FIGURE 1 Field ionization (a) and electron impact ionization (b) mass spectra of 1,1,3,3-tetramethyl-2-thiocarbonylcyclohexane *S*-oxide

Collision activation (c.a.) spectra were obtained by introducing helium as the collision gas *via* a needle valve into the second field free region between the magnetic and electric sector of the mass spectrometer. The collision gas was admitted as a molecular gas beam focused on the ion beam just behind the intermediate focus slit. Appropriate adjustment of the magnetic field secures passage of only the desired ion through this slit. The c.a. spectra of the single ions were then obtained by scanning the electric field.

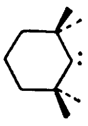
Owing to the relatively fast evaporation of the samples in the injection block (5—10 s) the mass spectra were recorded with a scan rate of 50—100 a.u. s^{-1} (signal : noise > 1 000), and the c.a. spectra within 5 s (signal : noise *ca.* 50).

The paramount advantage of the use of field ionization mass spectrometry as a detection system is to be sought for in the field ionization principle.[11] Since field ionization takes place with no excess energy, excluding polarization by the electric field, to the neutral molecule,[11a] it gives rise to molecular ions, even of very unstable substances, accompanied only by few, if any, fragment ions, in general of low intensity (<1%).[11b] In contrast electron impact mass spectrometry may produce very complicated electron impact-induced fragmentation patterns; this may be further confusing in cases where they are to be described as superpositions of electron impact mass spectra of several, often unknown, thermolysis products. This difference is clearly elucidated in Figure 1, depicting the field ionization and 70 eV electron impact mass spectra of the thioketen *S*-oxide (3).

Further structural information on the reaction products may be obtained by the additional recording of the c.a. spectra of the single field ionized molecules,[12] as the collision of field ionized molecules of high kinetic energy with neutral target atoms (*e.g.* He) is known to give rise to a large variety of fragments. In general these types of fragmentations resemble those formed under normal 70 eV electron impact conditions.[12] Furthermore, in cases of stable reaction products a direct comparison of the c.a. spectra with those of authentic samples can be carried out.

RESULTS

A priori, a variety of products can be expected by thermolytic decomposition of (3): the carbenes (4) and (5), with molecular ions of 138 and 150, respectively, the ketone (6) (*M* 154), the keten (7) (*M* 166), the thioketone (8) (*M* 170), the thioketen (9) (*M* 182), and the oxathiiran (10) (*M* 198), together with unchanged starting material (3) (*M* 198).



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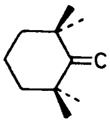

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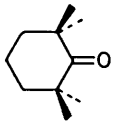

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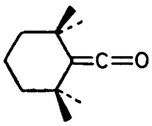

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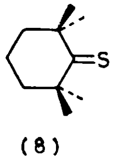

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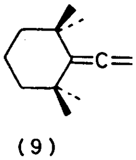
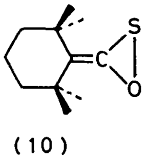


(9)



(10)

A wide range of ferromagnetic materials with Curie points from room temperature to *ca.* 1 400 K are readily available. We have studied the thermolytic decomposition of (3) at six temperatures in the 423—1 043 K range. The field ionization mass spectra obtained following thermolysis at these six temperatures are depicted in Figure 2.

Relative yields, expressed as mole fractions, of compounds (3)—(9) as a function of thermolysis temperature [a]

		Thermolysis temperature (K)					
Compound	*F* [b]	423	631	753	783	883	1 043
(3)	0.80 ± 0.13	1.00	1.00	0.11 ± 0.02	0.03 ± 0.005	0.04 ± 0.005	0.01 ± 0.002
(4)	0.90 ± 0.17 [c]	<0.01	<0.01	<0.01	<0.01	0.01 ± 0.002	0.03 ± 0.006
(5)	0.90 ± 0.17 [d]	<0.01	<0.01	<0.01	<0.01	0.03 ± 0.006	0.42 ± 0.08
(6)	1.13 ± 0.13	<0.01	<0.01	0.01 ± 0.001	0.01 ± 0.001	0.01 ± 0.001	<0.01
(7)	2.65 ± 0.54	<0.01	<0.01	0.18 ± 0.04	0.15 ± 0.03	0.13 ± 0.03	0.17 ± 0.03
(8)	1.35 ± 0.14	<0.01	<0.01	0.27 ± 0.03	0.16 ± 0.02	<0.01	<0.01
(9)	0.67 ± 0.06	<0.01	<0.01	0.42 ± 0.04	0.64 ± 0.06	0.78 ± 0.07	0.37 ± 0.03

[a] Yields are corrected for the amount of impurities present in the starting material. [b] The *F* factor (reciprocal field ionization weight sensitivity) is the value by which the actual observed peak height must be multiplied to give the amount of substance corresponding to the signal. [c] *F*(4) assumed to be equal to *F*(5). [d] *F*(5) calculated indirectly from the partial thermal decomposition of (9) (see Figure 3).

The spectra can be assigned to mixtures of compounds (4)—(9). It should be noted that the isotopic patterns may give valuable information, *e.g.* compounds (5)—(7) have evidently eliminated sulphur, since only iostopic clusters corresponding to ^{13}C and ^{18}O are seen, whereas the characteristic ^{34}S isotopic peaks are lacking. Furthermore, the identity of (8) and (9) was confirmed by comparison of the c.a. spectra of the single field ionized molecules with those obtained from authentic samples.[13] Unfortunately, it is not possible to detect small inorganic fragments, owing to the very low field ionization weight sensitivity of these compounds.*

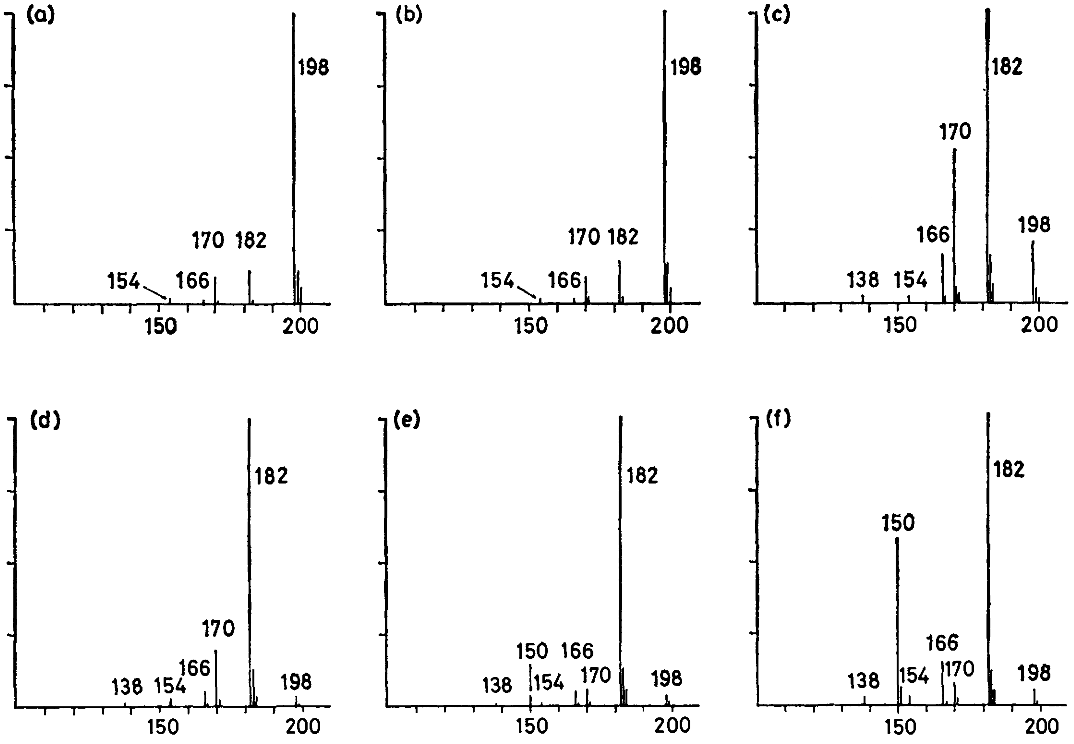


FIGURE 2 Field ionization mass spectra of 1,1,3,3-tetramethyl 2-thiocarbonylcyclohexane *S*-oxide following thermolysis at (a) 423, (b) 631, (c) 753, (d) 783, (e) 883, and (f) 1 043 K

It is not possible to calculate the yields of the single species directly from the field ionization mass spectra, as the individual compounds may exhibit rather different sensitivities.[11] However, by scanning mixtures of compounds (6)—(9) using varying mutual ratios, the individual relative weight sensitivities were calculated (see Table). The sensitivity of the vinylidene carbene (5) was calculated indirectly as 1.11, based on the partial decomposition of the thioketen (9) at 1 043 K (Figure 3b). We further assumed the sensitivity of the carbene (4) to be equal to that of (5).

As seen from Figure 1a the thioketen *S*-oxide (3) contained minor amounts of (7)—(9) as impurities. Equal amounts of these compounds are detected upon thermolysis at 423 and 631 K (Figures 2a and b) indicating that no decomposition takes place at these temperatures. Using the relative field ionization weight sensitivities we calculated the relative yields of the individual compounds formed at

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* Furthermore, the geometry of the ion source may play an important role (see ref. 11*b*).

higher temperatures, expressed as mole fractions, corrected for the initial content of impurities in the starting material. The results are given in the Table.

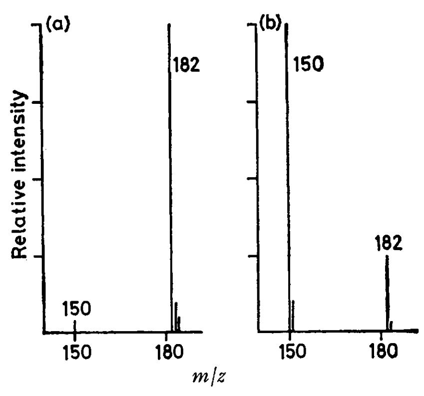
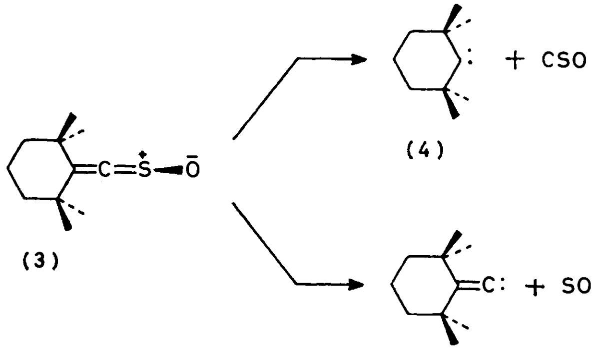


FIGURE 3 Field ionization mass spectra of 1,1,3,3-tetramethyl-2-thiocarbonylcyclohexane following thermolysis at (a) 883 and (b) 1 043 K

DISCUSSION

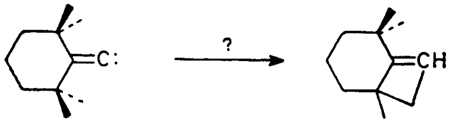
Easiest to explain is the formation of the carbenes (4) and (5), which apparently are generated by simple ruptures of the C=C and C=S bonds, respectively. Unfortunately, as mentioned above, field ionization suffers by the inability to detect small inorganic fragments, *e.g.* CSO and SO.



(3) (4) (5)

The formation of the vinylidene carbene (5) takes place at a markedly lower temperature than that of (4) in agreement with a lower C=S bond energy relative to that of the C=C bond.* Furthermore, it should be noted that the high yield of the carbene (5) found by thermolysing (3) at 1 043 K (Table) may originate from two sources, as the thioketen (9) at 1 043 K extrudes sulphur in high yield (Figure 3b). However, almost no sulphur extrusion from (9) was observed for thermolysis at 883 K (Figure 3a). Based on the field ionization mass spectra depicted in Figures 2f and 3b we have estimated the extent of further thermolysis of (9) to be <15% On the other hand, it is generally believed [10,14] that the very short contact times (*ca.* 10^{-3}—10^{-4} s) assure detection only of the primary products. Thus, we tentatively suggest that the major part of (5) originates directly from the *S*-oxide (3). Finally, it should be mentioned that the thioketen (9) is the only product found to undergo further thermolysis within the temperature range studied.

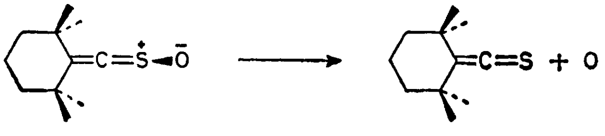
It should be noted that although we describe the products (4) and (5) as carbenes here they may well be isomeric structures, as *e.g.* (5) can undergo an easy intramolecular insertion reaction.[15] Nevertheless, we find support for the carbene structure by studying the relative field ionization weight sensitivities (Table), which are found to be comparable for the ketone (6) and the carbenes, since compounds with non-bonding electrons in general exhibit much higher weight sensitivities than pure hydrocarbons.[11b]



(5)

Additionally, it can be noted that the carbene (5) when generated in solution, does not undergo intramolecular insertion.[13b]

Surprisingly the major product from the gas-phase thermolysis of (3) in the temperature range 753—883 K is



(3) (9)

the corresponding thioketen (9), apparently formed by simple extrusion of atomic oxygen. Some reports on atomic oxygen extrusion have appeared, *e.g.* it is well known that pyridine *N*-oxide in the gas phase is photolytically deoxygenized.[16] Several other thermal and photolytic reactions, in the gas phase as well as in solution, could also be explained by atomic oxygen extrusion.[7,17] However, in these cases the reactions were carried out under circumstances where it was not possible to exclude bimolecular reactions. To our knowledge the reaction reported here is the first example of a thermally induced unimolecular atomic oxygen extrusion from an organic *S*-oxide.[1] The apparently large decrease in the yield of (9) by changing the thermolysis temperature from 883 to 1 043 K (Table) is explained by the occurence of the concurrent SO extrusion reaction, leading to the carbene (5).

Since none of the products (6)—(8) can be formed by simple bond rupture mechanisms, we formulate, by analogy with the thermal decomposition of thioketone *S*-oxides,[3,18] a primary ring closure into the methylene-oxathiiran (10). However, oxathiirans are, as mentioned previously, thermally highly labile compounds,[3-6] *e.g.* the decomposition of 3,3-diphenyloxathiiran has been studied by a flash photolytic study of diarylsulphines,[6]

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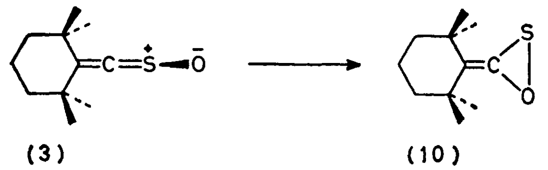
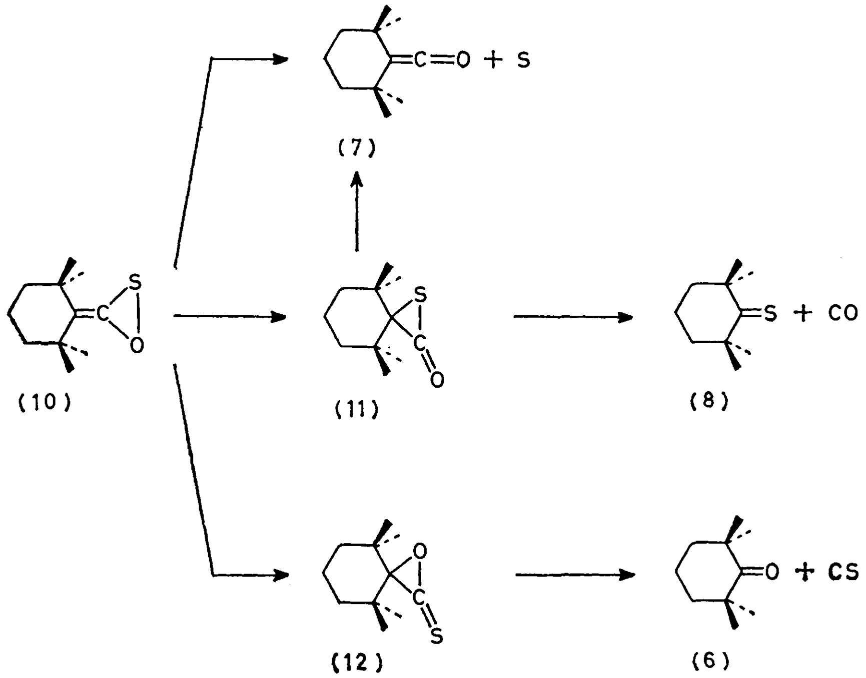
* E_{bond}(C=C) 611.2 kJ mol^{-1} (*cis*-but-2-ene: R. W. Alder, R. Baker, and J. M. Brown, 'Mechanism in Organic Chemistry,' Wiley, London, 1971, p. 7; E_{bond}(C=S) 540.0 kJ mol^{-1} ('Thioformaldehyde,' S. W. Benson, *Chem. Rev.*, 1978, **78**, 23).

the half-life being estimated to 1.3×10^{-3} s (in acetonitrile at room temperature). The diaryloxathiirans decompose quantitatively into the corresponding ketones and elemental sulphur upon thermolysis.[3-6] With this



background the formation of the keten (7) is easily explained by sulphur extrusion from the oxathiiran (10). On the other hand, it has also been reported that oxathiirans may rearrange into the corresponding thio-esters.[4,18] In the present case, with a methylene-oxathiiran such as (10), this rearrangement would cause formation of cyclic esters, α-thiololactones, and/or α-thionolactones. Recently Schaumann and Behrens[13a] reported the α-thiololactone (11) as the product from the nitrone oxidation of the thioketen (9). The compound was found to be thermally unstable, decomposing at 348 K (tetrachloromethane) entirely to the thioketone (8) and carbon monoxide.[13a] We have studied the gas-phase thermolysis of (11) at different temperatures. The compound was highly labile under these conditions, decomposing even at the lowest possible thermolysis temperature, 423 K, completely into a mixture of the thioketone (8), formed by CO extrusion, and the keten (7), apparently generated by loss of elemental sulphur.[*], [†] However, no reports on the isomeric α-thionolactone structure (12) have, to our knowledge, appeared, but by analogy with the decomposition of (11) we tentatively assume that (12) either spontaneously rearranges into (11) or extrudes carbon monosulphide to form the ketone (6).[‡] In recent reports on oxathiiran rearrangements[4,18] migration to sulphur is found to be predominant relative to migration to oxygen, in excellent agreement with the very low yield of the ketone (6) and the much higher yield of the corresponding thioketone (8), the former tentatively being described as a result of migration to oxygen.

In summary we rationalize the oxathiiran decomposition as in the Scheme.



SCHEME

Taking the sum of the yields of (6)—(8) (see Table) as an expression of the total amount of primarily formed oxathiiran (10), it can be seen that the two concurrent primary reactions, atomic oxygen extrusion and oxathiiran formation, both proceed to an almost equal extent at 753 K. An increase of the thermolysis temperature results in an increase in atomic oxygen extrusion with an equivalent simultaneous decrease in oxathiiran formation. However, the formation of the vinylidene carbene (5) at 1 043 K should be taken into account in order to maintain the overall (9) : (10) ratio (Figure 4). These variations may be described as a reflection of the concurrence of kinetically controlled oxathiiran formation and thermodynamically controlled extrusion of atomic oxygen.

Similarly the decomposition of the oxathiiran (10)

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[*] 423 K corresponds to the temperature of the heated line-of-sight inlet system, *i.e.* complete thermal decomposition of possible formed α-thiololactone (11) can be expected.

[†] Some temperature effects on the thioketone : keten ratio are found; the overall result, however, is independent of the thermolysis temperature.

[‡] A theoretical investigation on the potential energy surface of the possible α-thiololactone–α-thionolactone interconversion is in progress (L. Carlsen, to be published).

may be expressed in terms of kinetically *versus* thermodynamically controlled processes, the former leading to (8) [found to be present only for thermolysis at 753 and 783 K (Table)] *via* the strained three-membered ring (11), the latter to the sulphur-extrusion product, the keten (7).

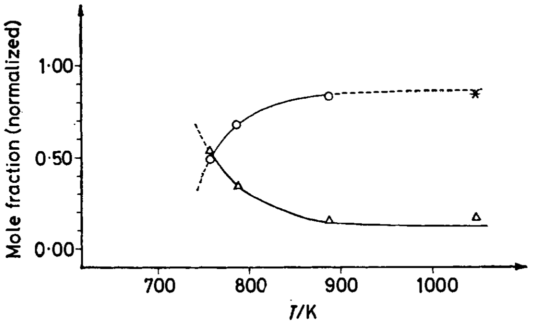

FIGURE 4 Molar fractions (normalized) of oxathiiran (10) (Δ) and thioketen (9) (○) as a function of thermolysis temperature. The point X corresponds to the theoretical amount of thioketen taking the amount of carbene (5) into account

Conclusions.—The gas-phase thermolytic decomposition of the thioketen *S*-oxide (3) affords a variety of products. The product ratios, which are highly dependent on the thermolysis temperature, can, however, be rationalized by the existence of only two concurrent primary processes (a) extrusion of atomic oxygen, whereby the thioketen (9) is formed, and (b) electrocyclic ring closure to the methyleneoxathiiran (10), the latter being followed by several consecutive concurrent reactions leading to the compounds (6)—(8). At higher temperatures further concurrent primary reactions must be taken into account, *i.e.* the formation of the carbenes (4) and (5) by simple bond rupture mechanisms.

We are indebted to Mrs. J. Funck for her careful preparation of the drawings.

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