Reaction of 1,3-Dienes with Sulphur Dioxide. Part 1. Thermal Decomposition of 2,5-Dihydrothiophen 1,1-Dioxides

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Rates of decomposition of 18 substituted dihydrothiophen 1,1-dioxides in solution (to yield the corresponding butadiene and SO_2) are reported, together with activation parameters and solvent and isotope effects. Rates are mildly accelerated by $+M$ groups at C-3 and by alkyl substituents at C-2 but sterically retarded by bulky groups at C-3 and especially by two β-substituents. 3,4,5,6-Tetrahydro-1*H*-cyclopenta[*c*]thiophen 2,2-dioxide is especially reactive and this is attributed to strain release during fragmentation. The reactions accord in general with requirements for a chelotropic reaction.

THE addition of sulphur dioxide to 1,3-dienes to form 2,5-dihydrothiophen dioxides (sulpholens) and the regression of this reaction at higher temperatures are generally believed to fall into the category of six-electron [4 + 2] cycloadditions.[1] Evidence for this mechanism includes the observation [2] that the reaction is accompanied by disrotation at either terminus of the

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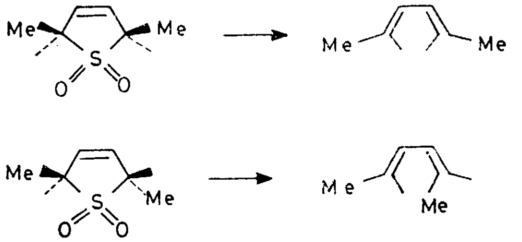
[1] R. B. Woodward and R. Hoffmann, 'The Conservation of Orbital Symmetry,' Verlag Chemie–Academic Press; G. B. Gill and M. R. Willis, 'Pericyclic Reactions,' Chapman and Hall, 1974.

[2] W. L. Mock, *J. Amer. Chem. Soc.*, 1975, **97**, 3666; 1966, **88**, 2859.

diene system. The orbital symmetry conservation principle predicts chelotropic reactions of this type will proceed by a suprafacial–suprafacial mode with disrotation. This reaction is of use in preparative chemistry in the purification of 1,3-dienes *via* the crystalline sulphones and for controlling their stereochemistry. Thus, a mixture of *cis*- and *trans*-piperylene gives only one sulpholen on reaction with sulphur dioxide and this decomposes entirely to the *trans*-diene.[3] Furthermore, the reaction might be useful as a means of selectively removing sulphur dioxide from a gas stream or from solution using a suitably reactive diene on a solid phase support. This would be capable of regeneration at an elevated temperature. In order to investigate the feasibility of this scheme, information was required on both forward and backward rates of the diene–SO_2 reaction. Little information is available hitherto as to the effects of structure on rates of addition or decomposition. Some sulpholen decomposition rates have been reported by Grummitt *et al.*[4] for methyl derivatives in the molten state, and extended to 3-phenyl-2,5-dihydrothiophen 1,1-dioxide.[5] Drake *et al.* have reported equilibrium constants for the reversible decomposition of some simple sulpholens.[6] More recently, Mock[7] has determined rates and activation parameters for decompositions of *cis*- and *trans*-2,5-dimethylsulpholens. We now report rates and relevant thermodynamic parameters for the decompositions of a wide variety of sulpholens, including the effects of solvent and isotopic substitution. Corresponding studies on the additions of SO_2 to the dienes will be published subsequently.



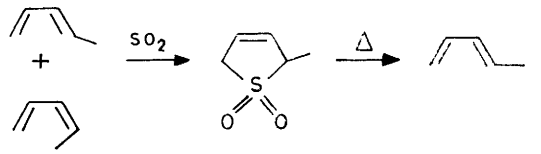


Table 1

Properties of butadienes and the corresponding 2,5-dihydrothiophen 1,1-dioxide

Butadiene substituent	B.p. (°C) [*p*/mmHg] Found	B.p. (°C) [*p*/mmHg] Lit.	Dihydrothiophen dioxide	M.p. (°C) Found	M.p. (°C) Lit.
None			(1)	64	64.5 [a]
2-Chloro	59		(7)	100.5	100.5 [b]
2-Methyl	34	34	(2)	63	63 [a,c]
2-Ethyl	66	66 [j]	(3)	57—58	
2-Isopropyl	83	83—85 [p]	(4)	42—43	
2-t-Butyl	100	100	(5)	82—83	82—83 [d]
2,3-Dimethyl	68—69		(13)	135	135 [a]
2-Phenyl	51 [0.4]	60 [13] [n]	(9)	133	133 [d]
1-Methyl	42		(16)	Liquid	Liquid [e]
2-*p*-Tolyl	78 [1.5]	50 [0.5] [l]	(10)	148	
2-*p*-Methoxyphenyl	83 [1]	80 [3] [m]	(11)	130	
2-*p*-Bromophenyl	83 [1.5]		(12)	167	
2-Bromomethyl			(8)	88	88 [f]
2-Neopentyl	28 [30]	62 [87] [k]	(6)	91	91—92 [g]
2,3-Tetramethylene	62 [68]	60 [95] [i]	(14)	93	
2,3-Trimethylene	45 [100]	45 [100] [h]	(15)	145—146 (decomp.)	

[a] Ref. 4. [b] R. L. Frank, C. E. Adams, R. J. Blegen, R. Deaun, and P. V. Smith, *Ind. and Eng. Chem.*, 1947, **39**, 887. [c] H. J. Backer and T. A. H. Blass, *Rec. Trav. chim.*, 1942, **54**, 785. [d] H. J. Backer and J. Strating, *Rec. Trav. chim.*, 1934, **53**, 525. [e] R. C. Krug and J. A. Rigney, *J. Org. Chem.*, 1962, **27**, 1305. [f] R. C. Krug and T. F. Yen, *J. Org. Chem.*, 1956, **21**, 1441. [g] D. Craig, J. J. Shipman, and R. B. Fowler, *J. Amer. Chem. Soc.*, 1961, **83**, 2885. [h] A. T. Blomquist, J. Wolinsky, Y. C. Meinwald, and D. T. Longone, *J. Amer. Chem. Soc.*, 1956, **78**, 6057. [i] W. Bailey and H. R. Golden, *J. Amer. Chem. Soc.*, 1953, **75**, 4780. [j] C. Marvel and J. L. R. Williams, *J. Amer. Chem. Soc.*, 1948, **70**, 3842. [k] A. T. Blomquist and J. C. Westfahl, *J. Amer. Chem. Soc.*, 1952, **74**, 4073. [l] C. C. Price, F. L. Benton, and C. J. Schmidle, *J. Amer. Chem. Soc.*, 1949, **71**, 2860. [m] E. A. Braude, E. R. H. Jones, and E. S. Stern, *J. Chem. Soc.*, 1947, 1087. [n] C. S. Marvel and R. G. Woodford, *J. Org. Chem.*, 1958, **23**, 1658. [p] C. S. Marvel, R. L. Myers, and J. H. Saunders, *J. Amer. Chem. Soc.*, 1948, **70**, 1694.

EXPERIMENTAL

The sulpholens were prepared by the reaction of the corresponding dienes with sulphur dioxide.[8] Reactive dienes were converted by passing a stream of the gas into a solution of the diene in ether, allowing to stand, and removing the ether. Less reactive or volatile dienes were sealed with an excess of liquid SO_2 in a steel vessel in which they were allowed to remain for up to 14 days. A crystal of hydroquinone was added to minimise polymer and polysulphone formation. The sulpholens were usually solids and were recrystallised to constant m.p. The liquid sulpholens were

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[3] S. D. Turk and R. L. Cobb, '1,4-Cycloadditions,' ed. J. Humer, Academic Press, New York, 1967, ch. 2.

[4] O. Grummitt, A. E. Ardis, and J. Fick, *J. Amer. Chem. Soc.*, 1950, **72**, 5167.

[5] O. Grummitt and H. Leaver, *J. Amer. Chem. Soc.*, 1952, **74**, 1595; O. Grummitt and J. Splitter, *ibid.*, p. 3924.

[6] L. R. Drake, S. C. Stowe, and A. M. Partansky, *J. Amer. Chem. Soc.*, 1946, **68**, 2521.

[7] W. L. Mock, *J. Amer. Chem. Soc.*, 1975, **97**, 3673.

[8] K. Alder, 'Newer Methods of Preparative Organic Chemistry,' Wiley–Interscience, New York, 1948, p. 381.

distilled under reduced pressure. The properties of the sulpholens used are recorded in Table 1. Butadiene, isoprene, chloroprene, piperylene, and 2,3-dimethylbutadiene were commercial samples used without further purification. 2-Ethylbutadiene and 2-isopropylbutadiene were prepared by the Wittig reaction.[9] Thus, 2-ethylacrolein [10] (18.0 g, 0.22 mol) was added to methylenetriphenylphosphorane in dimethyl sulphoxide (200 ml) prepared from methyltriphenylphosphonium bromide (80 g, 0.24 mol) and sodium hydride (5.8 g, 0.24 mol). The mixture was stirred under nitrogen at 0° for 10 min, then at room temperature for a further 45 min. 2-Ethylbutadiene was distilled out under reduced pressure and distilled in the presence of hydroquinone and was collected (13.5 g, 75%) at 66° (lit.,[11] 65—66°). In an analogous manner using isopropylacrolein, 2-isopropylbutadiene was prepared, b.p. 83°, in 70% yield. 2-t-Butylbutadiene was prepared by the action of vinylmagnesium bromide on an equimolar quantity of pinacolone in ether. The intermediate alcohol was isolated and dehydrated by slow distillation in the presence of 2% toluene-*p*-sulphonic acid and t-butylbutadiene (70%) was obtained, b.p. 100°. 2-Phenylbutadiene was prepared in analogous fashion using acetophenone in place of pinacolone. Dehydration was accomplished by distilling 2-phenylbut-3-en-2-ol in the presence of 5% potassium hydrogen sulphate at 10 mmHg under nitrogen. 2-Phenylbutadiene distilled out at 51° in 80% yield, and was redistilled under vacuum. Neopentylbutadiene was prepared according to the method of Blomquist and Westfahl.[12] Dimethylenecyclohexane [13] and dimethylenecyclopentane [14] were prepared by recorded methods. The substituted phenylbutadienes were prepared from the appropriate acetophenones by the Grignard procedure used for the parent compound.

Solvents were commercial and were purified; diphenyl ether was distilled, b.p. 79° at 0.07 mmHg, and then subjected to fractional freezing until it had m.p. 27°. Benzophenone, *N*-acetylbenzylamine, and stearic acid were recrystallised and had m.p. 46, 61, and 72° respectively. Other solvents were distilled at reduced pressures and collected at the b.p.

Kinetic measurements were made as follows. Pure sulpholen (0.04—0.08 g) with a crystal of hydroquinone was placed in a glass vessel (25 ml) and solvent (10 ml) added. A tube bearing a sintered disc reached almost to the bottom of the vessel and a gas outlet was provided at the top. It was completely immersed in an oil thermostat maintained constant to ±0.1° and preheated nitrogen was passed in to sweep out sulphur dioxide as it was formed. The effluent gases were bubbled through standard acid dichromate solution (200 ml) and the concentration of chromium(VI) at $\lambda_{max.}$ 350 nm ($\varepsilon_{max.}$ 2 330.9) was monitored. Tests showed that reproducible rates could be obtained, that quantitative absorption of SO_2 occurred, and at least 95% of the theoretical amount of sulphur dioxide was obtained, the remainder being accounted for in the formation of polymeric sulphones. At least two kinetic runs at each temperature were made and first-order rate constants were determined and averaged by a least-squares procedure as were the activation parameters. Details are in Supplementary Publication No. SUP 21798 (3 pp.).*

RESULTS AND DISCUSSION

Kinetic measurements were carried out at several temperatures for each compound studied over 2—3 half-lives. Rates were all found to obey accurately a first-order law and correlation coefficients for rate and Arrhenius plots were usually better than 0.999 0. For almost all the compounds studied, decomposition rates fall within a span of less than an order of magnitude. In general most substituents at C-3, irrespective of their nature, bring about a small decrease in rate. Two β-substituents cause a much greater decrease in rate which suggests that steric effects of β-substituents may be important.

An analysis of structural effects on the rates may be made by correlation analysis in order to investigate both electronic and steric effects of substituents. In the simplest scheme available, a Hammett plot was made for the *para*-substituted 3-phenylsulpholens. Increasing donor properties of the substituent appears to bring about a mild and rather irregular increase in rate but, with the limited amount of data, a rather poor fit to the Hammett equation is found with ρ *ca.* -1 ± 0.5 There was no perceptible correlation of rates with the Taft [15] aliphatic substituent constants, σ^*, which measure mainly electronic effects of the substituent groups. Consequently we carried out a multicorrelation analysis based on a best fit to equation (1) where σ_I and σ_R are inductive and

$$\log k/k_0 = \alpha\,\sigma_I + \beta\,\sigma_R + \gamma u + h \qquad (1)$$

resonance components of the substituent constants, the former being values given by Charton [16] and the latter defined by equation (2) using values of σ_p from ref. 17.

$$\sigma_R = \sigma_p - \sigma_I \qquad (2)$$

The steric parameters, *u*, based on van der Waals radii of the groups are those given by Charton [16] and *h* is a constant. Computed best fits using one, two, or all three parameters were made and the results are set out in Table 2. None of the individual parameters in any way

TABLE 2

Multicorrelation analysis of rate data

Independent variable(s)	Multicorrelation coefficient
σ_I	0.712 9
σ_R	0.565 9
u	0.784 8
$\sigma_I + \sigma_R$	0.727 9
$\sigma_I + u$	0.932 2
$\sigma_R + u$	0.981 7
$\sigma_R + \sigma_I + u$	0.992 0

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* For details of Supplementary Publications see Notice to Authors No. 7 in *J.C.S. Perkin II*, 1975, Index issue. Items less than 10 pp. are supplied as full-size copies.

[9] A. Maerker, *Org. Reactions*, 1965, **14**, 270.

[10] C. S. Marvel, R. L. Myers, and J. H. Saunders, *J. Amer. Chem. Soc.*, 1948, **70**, 1694.

[11] C. S. Marvel and J. L. R. Williams, *J. Amer. Chem. Soc.*, 1948, **70**, 3842.

[12] A. T. Blomquist and J. C. Westfahl, *J. Amer. Chem. Soc.*, 1952, **74**, 4073.

[13] J. G. Wichlatz and J. N. Short, U.S.P. 2,601,075/1952 (*Chem. Abs.*, 1952, **47**, 4367).

[14] W. J. Bailey and W. R. Sorenson, *J. Amer. Chem. Soc.*, 1954, **76**, 5421.

[15] R. W. Taft in 'Steric Effects in Organic Chemistry,' ed. M. S. Newman, Wiley, New York, 1956.

[16] M. Charton, *Progr. Phys. Org. Chem.*, 1973, **10**, 81.

[17] H. C. Brown and D. McDaniel, *J. Org. Chem.*, 1958, **23**, 420.

TABLE 3

Activation parameters for thermolysis of dihydrothiophen dioxides in diphenyl ether

Compound	log A	E_a/kcal mol^{-1}	ΔH/kcal mol^{-1}	ΔS/cal mol^{-1} K^{-1}	r *
(1)	14.4	32.3 ± 0.15 †	31.5	4.8	0.999 9
(2)	13.63	31.3 ± 1.2	30.5	1.24	0.998 8
(3)	14.3	32.6 ± 1.6	31.8	4.3	0.998 0
(4)	15.3	34.2 ± 0.5	33.4	8.9	0.999 7
(5)	13.2	31.2 ± 1.0	30.4	−0.74	0.998 7
(6)	14.1	32.0 ± 1.9	31.2	3.3	0.996 3
(7)	13.9	31.3 ± 1.0	30.5	2.54	0.998 8
(8)	13.8	31.7 ± 2.1	30.9	2.2	0.995 0
(9)	13.7	31.4 ± 2.2	30.6	1.62	0.995 0
(13)	13.3	31.5 ± 2.1	30.7	−0.33	0.999 7
(14)	13.1	27.3 ± 2.5	26.1	−1.08	0.991 0
(15)	13.3	31.4 ± 1.0	30.6	−0.11	0.999 0
(16)	13.2	28.4 ± 0.9	27.7	−0.83	0.999 0
(17) ‡			26.5 [a]		

	Data from ref. 4 [b]			Recalculated		
Compound	log A	E_a/kcal mol^{-1}	$\Delta S^‡$/cal mol^{-1} K^{-1}	log A	E_a/kcal mol^{-1}	$\Delta S^‡$/cal mol^{-1} K^{-1}
(1)	14.8	33.6	8.9	12.9	29.9	−2.2
(2)	15.0	34.6	9.9	14.6	33.7	5.8
(9)	18.8	43.5	27	18.7	43	24.2
(13)	14.78	35.4	8.4	11.8	29.7	−6.96
(16)	10.7	24.7	−10.1	9.3	22.3	−18.4

* Correlation coefficient for the Arrhenius plot. † Standard error. ‡ *cis*-2,5-Dimethyl-2,5-dihydrothiophen 1,1-dioxide. [a] From ref.7. [b] Measurements conducted in the absence of solvent.

may be said to follow trends in the reactivity but two parameter fits are better, notably those containing the steric factor, u. The best correlation is obtained using the full equation (1) and the resulting regression equation may be expressed as (3).

TABLE 4

Effect of solvent on the thermolysis of 3-methyl-2,5-dihydrothiophen 1,1-dioxide at 392.5 K

Solvent	$10^3 k_1$/min^{-1}	s (%)
n-Decane	7.00	0.4
Diphenyl ether	11.3	0.4
Benzophenone	12.6	0.8
Di-n-butyl phthalate	11.7	1.4
Sulpholan	12.8	1.2
None	6.04	1.8
Triethylene glycol	8.98	0.1
N-Acetylbenzylamine	6.8	0.3
Stearic acid	8.3	1.9

$$3 + \log k = 0.181\ \sigma_I - 1.463\ \sigma_R - 0.497\ u - 0.139 \quad (3)$$

With the somewhat limited set of data (eight compounds) used, it nonetheless appears clear that the most important of the three parameters is the steric factor (on account of the scaling difference in values of u and σ the coefficient of the former appears to be deceptively small), though electronic influences also play a part, particularly resonance interactions.

TABLE 6

Effects of solvent on activation parameters for decomposition of 3-methyl-2,5-dihydrothiophen dioxide

Solvent	T/K	k_1/min^{-1}	log (A/s^{-1})	E_a/kcal mol^{-1}	$\Delta H^‡$/kcal mol^{-1}	$\Delta S^‡$/cal mol^{-1} K^{-1}	r
Diphenyl ether	388	5.95	13.63	31.3	30.5	1.24	0.998 0
	392.5	11.35					
	408	42.2					
	412.5	66.0					
n-Decane	388	3.68	14.66	33.4	32.6	5.97	0.998 5
	392.5	7.00					
	402.5	20.2					
	412.5	50.3					

The decomposition rates of the aryl derivatives (Table 5) indicate that electron-donating substituents at C-3, other things being equal, modestly accelerate the reaction. The situation must be further complicated since electron-withdrawing groups such as Cl and CH_2Br also bring about increases in rate. Dissection of these effects reveals that this is due to a reduction in A rather than E_a. There seems little doubt that

TABLE 5

Relative thermolysis rates of dihydrothiophen 1,1-dioxides in diphenyl ether at 388 K

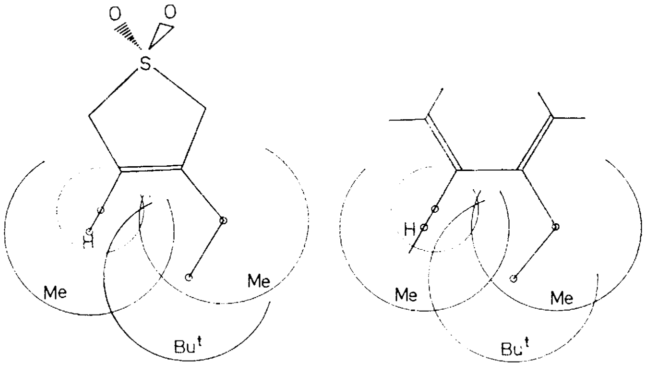
Compound	k_{rel}	Compound	k_{rel}
(1)	1.00	(11)	0.81
(2)	0.59	(12)	0.53
(3)	0.54	(13)	0.18
(4)	0.20	(14)	32.3
(5)	0.26	(15)	0.64
(6)	0.61	(16)	1.19
(7)	1.07	(17)	0.41 [a]
(8)	0.72	(18) *	0.064
(9)	0.54	(19) †	0.055
(10)	0.57		

[a] From ref. 7.

* 3-Bromomethyl-4-methyl-2,5-dihydrothiophen 1,1-dioxide.

† 3,4-Bisbromomethyl-2,5-dihydrothiophen 1,1-dioxide.

the size of β-substituents is important, the larger groups causing a reduction in rate which is particularly marked when two such substituents are present, at C-3 and -4, the *A* factor again being at least partly responsible. The origin of this steric effect is not obvious. Repulsive interactions between groups at C-3 and -4 in a planar system are already at a maximum unless during ring opening the two further approach each other. Scale diagrams (Figure) of the sulpholen and butadiene systems indicate a closer approach of two methyl groups of only *ca.* 1 pm during the whole course of the reaction providing that coplanarity is maintained, an amount hardly commensurate with the observed rate effect. The further possibility may be considered that the five-membered ring might assume sufficient non-planarity as to permit substituents at C-3 and -4 to assume a dihedral angle >0° thus relieving an eclipsing interaction. If coplanarity were a requirement of the reaction in order to maximise π-interactions, steric compression would accompany the activation process. Further information on the conformations of dihydrothiophen dioxides would be required to substantiate this.* The rates and activation parameters of the cyclohexa[*c*]thiophen analogue (15) are much the same as those for the dimethyl compound (13) but those for the cyclopenta[*c*]thiophen dioxide (14) show that the much greater reactivity is due to an activation energy lower by *ca.* 5 kcal mol^{-1}. It seems that this is likely to be due to the release of angle strain energy inherent in the system (*ca.* 12° per bond at the olefinic centre). There are, however no quantitative estimates of this nor of the strain energy of the parent hydrocarbon, bicyclo[3.3.0]oct-1(5)-ene. It seems probable that much less bond angle strain would exist in the homologue, bicyclo[4.3.0]nonene. It is worth noting that 1,2-dimethylenecyclobutane does not react with SO_2 possibly on account of the even larger strain engendered in a bicyclo[3.2.0]heptene system.



van der Waals distances between β-substituents in 2,5-dihydrothiophen 1,1-dioxides and the corresponding butadienes

2-Substituted didhydrothiophen dioxides are somewhat more reactive than the parent compound. A 2-methyl group should stabilise the diene to a greater extent than it does the sulpholen due to hyperconjugative interactions in the former. Steric effects may also aid the decomposition by relief of eclipsing interactions between the 2-substituent and the sulphone oxygen. This would not account for the large difference in rates between *cis*- and *trans*-2,5-dimethyldihydrothiophen dioxides.[7] Another factor which may affect the rates is the obstruction to the departure of the SO_2 molecule normal to the plane of the five-membered ring which is caused by 2-substituents. The *cis*-2,5-isomer presents one face free of substituents but the *trans*-isomer has none.

The Arrhenius activation energies and the enthalpies of activation (Table 3) are similar over a wide range of substituent variation. The reactive compounds (14), (16), and (17) show significantly lower values revealing that rate differences are due to this term. The activation entropies are all rather low considering this reaction involves the fragmentation of a molecule. In this connection it may be mentioned that values of activation parameters calculated from the rate data of Grummitt *et al.*[4,5] by equation (4) do not agree with the values quoted by these authors and subsequent workers.[2] The recalculated values from the earlier rate data also appear in Table 3. Considerable differences between these and our values are apparent. In particular, 3-phenylsulpholen (9) was previously reported to have an impossibly high value of log *A* (18) due possibly to the incursion of polymerisation or rearrangement to polysulphone in the absence of solvent. In solution, this compound behaved normally. The low values of $\Delta S^\ddagger$ (indeed some are negative) must indicate that at the transition state, little bond breaking has occurred, *i.e.* an early transition state along the reaction co-ordinate. This in itself may be insufficient to explain negative values and it seems reasonable to suppose that the transition state is more solvated than the reagent. Since little dipolar character appears to be developed as shown by the solvent effects upon rates it would be necessary to invoke donor–acceptor interactions to account for this solvation. This however does not seem unreasonable since SO_2 is an acceptor and the reactions appear to proceed at a faster rate in solvents which would have greater donor properties, *e.g.* ethers, ketones, esters > alcohols, amides > hydrocarbons, acids. In a general way the rates (Table 4) follow the expected donor numbers[18] of the solvents but not any 'polarity' scale;[19] the effects of changing solvent are, however, small. In accordance with this interpretation, the value of $\Delta S^\ddagger$ in solvent diphenyl ether is lower than in decane for decomposition of 3-methylsulpholen (Table 6). The closest analogy to our reaction is the thermal decomposition of cyclopent-3-enone which undergoes a concerted loss of carbon monoxide at *ca.* 600 K with $\Delta S^\ddagger$ 4.4 cal K^{-1} mol^{-1}, a similarly low value. Some retro-Diels–

$$\begin{aligned} \log A &= \log k + E_a/2.303\,RT \\ A &= kT/h\,e^{\Delta S^\ddagger/R} \end{aligned} \qquad (4)$$

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* *Note added in proof.* We have carried out a crystallographic analysis of 3,4-dimethylsulpholen and find that the methyl groups lie out of the plane of the 5-membered ring by 5—7°.

[18] N. S. Isaacs and E. Rannala, *J.C.S. Perkin II*, 1974, 902.

[19] E. M. Kosower, *J. Amer. Chem. Soc.*, 1958, **80**, 3253.

Alder reactions have also been studied such as the thermolysis of cyclohexene ($\Delta S^{\ddagger}$ 7.8 cal K^{-1} mol^{-1} [20]) and of bicyclo[2.2.2]octene ($\Delta S^{\ddagger}$ 8.5 cal K^{-1} mol^{-1}).[21] These values are all low compared with the total entropy change of the reaction, *ca.* 40 cal K^{-1} mol^{-1} and, allowing for their being in the gas phase, appear similar to the sulpholen decompositions.

Normal secondary deuterium isotope effects have been found for the decompositions of [2-^{2}H]sulpholen and for 3-methyl[2-^{2}H]sulpholen (k_H/k_D 1.02 and 1.06, respectively per deuterium atom) which accord with considerable rehybridisation of the β-carbon atoms in the transition state.[21] In conclusion, the thermolysis of sulpholens appears to occur by an essentially neutral concerted fission, insensitive to solvent and little affected by the electronic effects of substituents. It is more governed by steric effects, being retarded by β-substituents and accelerated by an α-group. For the purpose of SO_2 recovery from a diene used as a scavenger these facts would have to be considered in conjunction with the corresponding rates of addition to the diene which will be reported subsequently.

[5/2257 *Received, 18th November,* 1975]

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[20] D. Rowley and H. Steiner, *Discuss. Faraday Soc.*, 1957, **10**, 198.

[21] R. Walsh and J. M. Wells, *Internat. J. Chem. Kinetics*, 1975, **7**, 319.