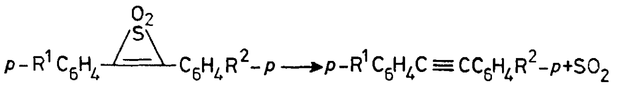
Sulphur Dioxide Extrusion from Substituted Thiiren 1,1-Dioxides

By J. CHRISTOPHER PHILIPS* and OSCAR MORALES
(*Department of Chemistry, University of Detroit, Detroit, Michigan* 48221)

Summary Rate data for sulphur dioxide extrusions from thiiren 1,1-dioxides correlate best with the sum of the $\sigma_p{}^+$ substituent constants and are consistent with a stepwise cleavage of the two carbon–sulphur bonds.

THE thermal decomposition of thiiren dioxides[1] is known to produce acetylenes and sulphur dioxide.[2] We now report data which show that electron-donating substituents facilitate the extrusion process. In addition the data suggest strongly that a stepwise, rather than a non-linear, symmetry-allowed, concerted extrusion mechanism[3] is operable. Table 1 summarizes rate constant data for the pseudo-first-order decompositions of *para*-substituted diphenylthiiren 1,1-dioxides in 95% ethanol.



(1)

TABLE 1. Rate constant data for thiiren dioxide decomposition 95% ethanol at 73 °C.

Compound	R^1	R^2	$k^a \times 10^4/s^{-1}$	$\Delta H^{\ddagger b}$/cal mol^{-1}	$\Delta S^{\ddagger b}$/cal K^{-1} mol^{-1}
(**1a**)	Me	Me	6·94 ± 0·08	26·1	2·1
(**1b**)	Bu^t	Bu^t	6·41 ± 0·12	—	—
(**1c**)	Me	H	4·74 ± 0·11	—	—
(**1d**)	Bu^t	H	4·12 ± 0·09	—	—
(**1e**)	H	H	1·85 ± 0·02	27·1	2·3
(**1f**)	Cl	Cl	1·43 ± 0·05	—	—
(**1g**)	Br	Br	1·34 ± 0·03	27·6	3·3

[a] Average of a minimum of six determinations with the standard deviation of the mean expressed at the 95% confidence level. The rate constants were determined by measuring the disappearance of the long-wavelength u.v. absorption of the thiiren dioxide. [b] Calculated from rate constant data determined at 63, 73, 82, and 93 °C.

Hammett plots of log *k vs.* various simple substituent constants afforded the best correlation when the sum of the Okamoto–Brown $\sigma_p{}^+$ values[4] was used (linear correlation; ρ — 0·86, correlation coefficient 0·98). That the rate data correlate best with the sum of the $\sigma_p{}^+$ substituent constants argues for developing positive charge on the three-membered ring carbon atoms in the transition state; however, such a correlation does not, *a priori*, differentiate between a stepwise zwitterionic process, a stepwise diradical process, or a concerted extrusion process. Preliminary measurements show only a minor dependence of the rate data on solvent polarity, and thus we prefer to consider only the latter two mechanisms in our discussion.†

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† Extrusion rate constants (10^4 k/s^{-1}) for (**1a**) at 73 °C in decane, absolute ethanol, 95% ethanol, and 50% dioxan–water 0·462, 4·76, 6·94, and 11·44.

The Hammett equation has proved surprisingly useful in correlating processes involving transition states with free-radical character.[5] The usual argument involves postulation of dipolar structures as resonance contributors to the overall transition-state species. With free-radical generation from substituted toluenes, ρ is generally negative; *i.e.*, the benzylic carbon acquires developing positive charge. The validity of this approach has been demonstrated well by Pryor[6] with the t-butyl radical as the hydrogen-abstracting species. In this case ρ is positive, *i.e.*, the localized, developing positive charge in the transition state is preferentially located on the t-butyl group because of its electronic nature, leaving the benzylic carbon of the substituted toluene with significant negative charge. In considering homolytic cleavage of a carbon–sulphur bond in (**1**), it does not seem surprising that the electron-withdrawing sulphonyl group acquires developing negative charge leaving partial positive charge associated with the vinylic carbon atom and resulting in the observed negative ρ value.

Either a concerted or a stepwise extrusion mechanism could afford such charge-development in the transition state and hence a negative ρ value. These two processes could possibly be differentiated from rate data for the series (**1b**), (**1d**), and (**1e**). A process in which both carbon–sulphur bonds are undergoing simultaneous cleavage should be affected by substituents in a multiplicative fashion,[7] *i.e.*, successive replacement of H by t-butyl groups should result in multiplicative rate enhancements with the rate constant for (**1d**) expected to be the geometric mean of that for (**1e**) and (**1b**).[8]

A stepwise cleavage of the two carbon–sulphur bonds also demands that (**1b**) should react faster than (**1d**) in this case because of a statistical factor. Here, the rate-enhancement factors for the substituents should be additive rather than multiplicative, and the rate constant for (**1d**) is expected to be the arithmetic mean of that for (**1e**) and (**1b**).[8] Table 2 summarizes observed and calculated rate constants in this series and in the related series (**1e**), (**1c**), and (**1a**).

TABLE 2. Observed and calculated rate constants for thiiren dioxide decomposition

Compound	$10^4\,k/\text{s}^{-1}$ values		
	Obs.	Calc.[a] (stepwise)	Calc.[b] (concerted)
(**1d**)	4·12	4·13	3·44
(**1c**)	4·74	4·40	3·58

[a] Arithmetic mean of the observed rate constants for (**1e**), (**1b**) and (**1e**), (**1a**). [b] Geometric mean of the observed rate constants for (**1e**), (**1b**) and (**1e**), (**1a**).

The observed rate constants for the mono-substituted thiiren dioxide in each series are significantly closer to the calculated values for the stepwise cleavage process and clearly provide evidence favouring this mechanism.‡

We thank the Research Corporation and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support, and Professor Jack Hine for helpful mechanistic discussions.

(*Received*, *7th March* 1977; *Com.* 216.)

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‡ Interpolation of the Hammett plot for a series of methoxy-derivatives suggests significantly larger variations in geometric and arithmetic mean values for such a series. Unfortunately, preparation of the requisite methoxy-substituted halogenosulphones has been thwarted by competitive Pummerer cleavage processes in the halogenation step. Other synthetic routes to these compounds are being investigated.

[1] The thiiren dioxides were prepared from the corresponding αα-dichlorodibenzyl sulphones: see J. C. Philips, J. V. Swisher, D. Haidukewych, and O. Morales, *Chem. Comm.*, 1971, 22.

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[5] See G. A. Russell, 'Free Radicals,' Vol. 1, ed. J. K. Kochi, Wiley, New York, 1973, Ch. 7, for discussion of this topic.

[6] W. A. Pryor, W. H. Davis, jr., and J. P. Stanley, *J. Amer. Chem. Soc.*, 1973, **95**, 4754; see also, R. W. Henderson and R. D. Ward, jr., *ibid.*, 1974, **96**, 7556; W. A. Pryor and W. H. Davis, jr., *ibid.*, p. 7557.

[7] P. G. Gassman and D. S. Patton, *J. Amer. Chem. Soc.*, 1969, **91**, 2160.

[8] See M. Taagepera and E. R. Thornton, *J. Amer. Chem. Soc.*, 1972, **94**, 1168, for a detailed discussion of these concepts.