

Heats of Oxidation of the Isomeric 3-t-Butylthietan 1-Oxides

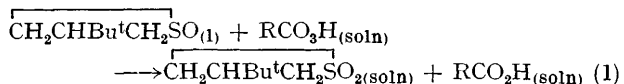
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Summary The *cis* and *trans* geometrical isomers of the 3-t-butylthietan 1-oxides have been isolated in quantity, and their enthalpies of oxidation to 3-t-butylthietan 1,1-dioxide have been measured directly.

EQUILIBRATION of the *cis* (I) and *trans* (II) 3-t-butylthietan 1-oxides at 170–175°C in decalin solution gives an 82–85:18–15 ratio of the two isomers,¹ corresponding to a free-energy difference of *ca.* 6.7 kJ mol⁻¹.

The isomers (I) and (II) have now been separated *via* fractional crystallisation, from ethanol, of their mercury II complexes and identified by dipole moment and other measurements.¹ Their enthalpies of oxidation to the same sulphone (III) were measured by allowing *ca.* 1 mmol of each to react with a ten-fold excess of perlauric acid² in benzene in the semi-micro reaction calorimeter previously described.³ The results refer to reaction (1). Heats of



oxidation ($-\Delta H$, kJ mol⁻¹) at 298 K are 315.34 ± 3.7 and 321.76 ± 1.5 for (I) and (II) respectively. The uncertainties are expressed as twice the standard deviation of the mean.

The difference, $\Delta(\Delta H)$, between the enthalpies of oxidation of (I) and (II) to (III) is 6.4 ± 3.7 kJ mol⁻¹ which overlaps the previously reported¹ free energy difference between the two isomers, $\Delta G = ca.$ 6.7 kJ mol⁻¹.

¹ C. R. Johnston and D. McCants, *J. Amer. Chem. Soc.*, 1964, **86**, 2935; J. E. Martin and J. J. Uebel, *ibid.*, 1964, **86**, 2936; C. R. Johnson and W. O. Siegl, *ibid.*, 1969, **91**, 2796.

² L. Silbert, D. Siegel, and D. Swern, *J. Amer. Chem. Soc.*, 1962, **27**, 1336.

³ M. A. Frisch and H. Mackle, *J. Sci. Inst.*, 1965, **42**, 186.

⁴ C. R. Johnson and W. O. Siegl, *Tetrahedron Letters*, 1969, 1879.

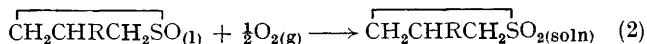
⁵ D. W. Scott, H. L. Finke, W. F. Hubbard, J. P. McCullough, C. Katz, M. E. Gross, J. F. Messerly, R. E. Pennington, and G. Waddington, *J. Amer. Chem. Soc.*, 1953, **75**, 2795.

⁶ H. A. Swain, L. A. Silbert, and J. G. Miller, *J. Amer. Chem. Soc.*, 1964, **86**, 2563.

⁷ T. B. Douglas, *J. Amer. Chem. Soc.*, 1946, **68**, 1072.

The assignment of a puckered ring structure to (I) and (II) has been suggested by Johnson and Siegl.⁴ It is true that spectroscopic and thermodynamic evidence⁵ indicates that the unsubstituted thiacyclobutane ring is planar, but small rapid ring inversion might be difficult to detect. Furthermore, the presence of the bulky t-butyl group in (I) and (II) may well make a particular ring conformation more rigid and the n.m.r. studies⁴ of Johnson and Siegl lead to this conclusion.

Swain *et al.*⁶ have estimated the heat of dissociation of peroxyauric acid in the gas phase to be 83.7 ± 12.5 kJ mol⁻¹. Thus the enthalpies of oxidation of the sulphoxides (I) and (II) are respectively -238 ± 14 and -231.8 ± 14 kJ mol⁻¹. These refer to reaction (2) and may be compared



with Douglas' result,⁷ -224.3 ± 8 kJ mol⁻¹, for reaction (3)



Similar studies on the corresponding six-membered ring isomers are envisaged, and we consider this approach to geometrical enthalpy differences to be widely applicable in situations where the isomers can be quantitatively converted to a common product.

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