Electron Spin Resonance Study of the t-Butylperthiyl Radical

By JOHN E. BENNETT and GEORGE BRUNTON*
(*Shell Research Ltd., Thornton Research Centre, P.O. Box* 1, *Chester* CH1 3SH)

Summary The e.s.r. spectrum attributed to the t-butylperthiyl radical, $Bu^tSS\cdot$, has been observed in solution; the radical is characterised by a single line, $\Delta H = 0{\cdot}4$ mT and $g_{iso} = 2{\cdot}025$, and it decays by a second-order process with a rate constant, $2k_t$, of 2×10^8 dm^3 mol^{-1} s^{-1} at -86 °C.

It is well established that alkoxyl[1] or alkyl thiyl radicals[2] cannot be detected by e.s.r. spectroscopy unless a specific interaction (*e.g.*, hydrogen-bonding[3]) exists to lift the degeneracy of the π-levels. The degeneracy can also be destroyed by delocalisation of the unpaired electron onto a second heteroatom. Thus alkyl peroxyl radicals, ROO•, can readily be detected in solution by e.s.r. spectroscopy.[4] We have found that a comparable situation pertains for sulphur-centred analogues, and that it is possible to observe the e.s.r. spectrum of an alkyl perthiyl radical, RSS•, in solution.

t-Butylthiosulphenyl chloride, Bu^tSSCl, was prepared from 1,1-dimethylethanethiol and sulphur dichloride and distilled under reduced pressure, b.p. 64 °C at 20 mmHg (lit.[5] b.p. 55—60 °C at 10 mmHg). *In situ* photolysis of a sample of the thiosulphenyl chloride in toluene at -86 °C produces a single line e.s.r. spectrum with $\Delta H = 0{\cdot}4$ mT and $g_{iso} = 2{\cdot}025 \pm 0{\cdot}001$, which we assign to the t-butylperthiyl radical, $Bu^tSS\bullet$.†

The g-value of the t-butylperthiyl radical is very similar to that (2·0262) of a radical detected during the photolysis of di-n-butyl disulphide.[6] The original assignment of this spectrum was to the n-butylthiyl radical, $Bu^nS\bullet$, but this has been questioned because of the improbability that alkyl thiyl radicals will be detected in solution.[7] On the basis of our result we suggest that the observed spectrum is more likely to arise from the n-butylperthiyl radical, $Bu^nSS\bullet$. This revised assignment is consistent with the proposal, based on product studies,[8] that alkyl perthiyl radicals are important intermediates during the photosensitised decomposition of disulphides in solution.

Under certain conditions, γ- or u.v.-irradiation of alkanethiols or disulphides in the solid state produces an anisotropic e.s.r. spectrum from an unknown sulphur-containing species, which is characterised[2] by g-values close to 2·058, 2·025, and 2·00 ($g_{av} = 2{\cdot}028$). Measurement of the ^{33}S hyperfine splitting in this species has established that the unpaired electron is delocalised over two sulphur atoms.[9] However the assignment of these spectra has been the subject of some controversy and two alternative structures for the radical species have been proposed; either RSS•,[9,10] or $RS^{\bullet}SR_2$.[2,7]

Arguments for and against both structures have been considered in some detail,[7] and although structural evidence from e.s.r. spectroscopy favours RSS• without exclusion of $RS^{\bullet}SR_2$, it is concluded that the chemical evidence is more consistent with formation of $RS^{\bullet}SR_2$. The g-value (2·025), which we have assigned to an alkyl perthiyl radical in solution, is close to the average g-value (2·026—2·029) for the unknown radical detected in the solid state. Photolysis of a sample of the t-butylthiosulphenyl chloride in a benzene or [$^2H_8$]toluene matrix at -196 °C produces an anisotropic e.s.r. spectrum with g-values of 2·059, 2·026, and 2·001 ($g_{av} = 2{\cdot}029$) which are virtually identical with those observed in the earlier work.[2,7] However the spectrum appears to arise from more than one radical and therefore it is not possible to make a positive identification of the solid state spectrum of the t-butylperthiyl radical under our experimental conditions. Thus although our results tend to support the assignment of the solid-state spectrum to the RSS• radical, we cannot finally resolve the ambiguity. Very recently the radical $CF_3S^{\bullet}SR_2$ has been detected in solution.[11] Its isotropic g-value is 2·0133, which is significantly lower than that expected for the unknown radical. However the ambiguity still remains, since the presence of the electronegative $-CF_3$ group rather than an alkyl group may well result in a significant decrease in the g-value.

We have also found that the t-butylperthiyl radical decays with second-order kinetics. At -86 °C the termination rate constant, $2k_t$, measured by kinetic e.s.r. spectroscopy (previously described in ref. 12) is 2×10^8 dm^3 mol^{-1} s^{-1}. This value is comparable with that measured for the t-butylsulphinyl radical, $Bu^tSO\bullet$, ($2k_t = 6 \times 10^7$ dm^3 mol^{-1} at -100 °C[13]) but is very much faster than the value (*ca.* 1 dm^3 mol^{-1} s^{-1}) for the isostructural t-butylperoxyl radical at a similar temperature.[14] The large difference in $2k_t$ between the t-butylperoxyl radical and the t-butylperthiyl radical reflects the difference in stability of the corresponding products of dimerisation. Di-t-butyl tetroxide is known[15] to be unstable above *ca.* -73 °C, whereas di-t-butyl tetrasulphide can be isolated.[8]

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† A referee has suggested the possible formation of $Bu^t(RS)S^{\bullet}SCl$ (R = Bu^t or Cl). Previous studies [W. B. Gara, B. P. Roberts, B. C. Gilbert, C. M. Kirk, and R. O. C. Norman, *J. Chem. Research*, (*S*), 1977, 152; (*M*), 1977, 1748] indicate that radicals of this type may readily undergo α-scission. Thus on the basis of the observed second-order kinetics we favour the assignment given above.

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