

An Electron Spin Resonance Study of the Reactions of Alkoxy and Trimethylsiloxy Radicals with Dialkyl Sulphoxides

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Qualitative and quantitative studies have been made of the dealkylation of dialkyl sulphoxides by t-butoxy and trimethylsiloxy radicals. Dimethyl sulphoxide undergoes $S_{\text{H}}2$ reaction at sulphur much less readily with $\text{Bu}^t\text{O}^\cdot$ than with HO^\cdot or $\text{Me}_3\text{SiO}^\cdot$. The rate of t-butoxydealkylation of symmetrical and of mixed dialkyl sulphoxides increases with the stability of the displaced alkyl radical, providing steric effects are not dominant. Siloxydealkylation of sulphoxides appears to be more rapid and less selective than t-butoxydealkylation, and it is suggested that the electrophilicity of the attacking oxy radical is an important factor in determining rate and selectivity.

The cyclic sulphoxides $\text{CH}_2[\text{CH}_2]_n\text{SO}$ ($n = 2-4$) undergo increasingly rapid ring opening as n decreases, a trend attributed to relief of angle strain.

No e.s.r. spectra of sulphuranyloxy radicals, $\text{R}_2\dot{\text{S}}(\text{O})\text{OX}$ or $\text{R}(\text{RO})\dot{\text{S}}(\text{O})\text{OX}$, were detected during the reactions of XO^\cdot with sulphoxides or with alkyl alkanesulphinates, respectively.

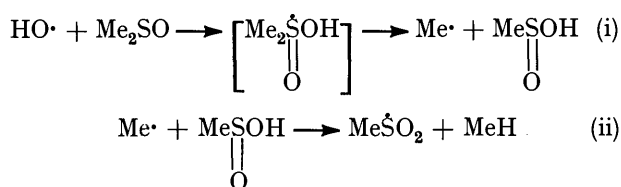
PULSE radiolysis studies¹ have shown that hydroxyl radicals react extremely rapidly ($k 7 \times 10^9 \text{ l mol}^{-1} \text{ s}^{-1}$ at

¹ G. Meissner, A. Henglein, and G. Beck, *Z. Naturforsch.*, 1967, **22b**, 13.

room temperature^{1,2}) with dimethyl sulphoxide (DMSO) in aqueous solution. Both methyl and methanesul-

² B. C. Gilbert, R. O. C. Norman, and R. C. Sealy, *J.C.S. Perkin II*, 1975, 303.

phenyl radicals have been detected by e.s.r. spectroscopy during the reaction of hydroxyl radicals (produced by the $\text{Ti}^{\text{III}}\text{-H}_2\text{O}_2$ couple) and DMSO in an aqueous flow system,²⁻⁴ and a two-step mechanism involving radical addition to sulphur followed by fragmentation of the intermediate adduct has been proposed to account for the formation of methyl radicals.²



Gilbert, Norman, and their co-workers⁵ have recently employed reaction (i) as the radical source in kinetic studies of the interaction of methyl radicals with organic molecules in aqueous solution. Using e.s.r. spectroscopy these authors have also demonstrated⁶ that reactions analogous to (i) and (ii) occur generally for higher dialkyl sulphoxides.

However, there is some evidence that t-butoxyl radicals react only sluggishly with DMSO.^{7,8} For example, although methyl radicals are produced when t-butoxyl radicals are generated in the presence of DMSO, it was shown^{7,8} [by using $(\text{CD}_3)_2\text{SO}$] that these arise from the β -scission of the t-butoxyl radicals and not from displacement at sulphur.

In order to clarify the situation we set out to investigate, using e.s.r. spectroscopy, the reactions of t-butoxyl and of trimethylsiloxy radicals with a range of dialkyl sulphoxides in non-aqueous solvents.

RESULTS

Reactions with t-Butoxyl Radicals.—Irradiation at 218 K of a solution containing di-t-butyl peroxide and DMSO in a mixture of 1,1,2-trichloro-1,2,2-trifluoroethane (freon) and t-butyl alcohol (1:1 by volume) as solvent, gave rise to weak e.s.r. spectra assigned to the radicals $\cdot\text{CH}_3$, $\cdot\text{CH}_2\text{S}(\text{O})\text{Me}$,⁹ and $\cdot\text{CH}_2\text{CMe}_2\text{OH}$. However, a similarly weak spectrum of the methyl radical was detected when the peroxide was omitted from the mixture, and we conclude that photochemical cleavage of the C-S bond may be the major source of methyl radicals from DMSO. In the presence of peroxide no signal which could be assigned to the adduct radical $\cdot\text{SMe}_2(\text{O})\text{OBu}^t$ was detected, even at 168 K in ethylene oxide as solvent.

The higher sulphoxides were more soluble; and irradiation of a mixture of di-t-butyl peroxide and diethyl sulphoxide in freon yielded overlapping spectra of the radicals $\text{Et}\cdot$ and $\cdot\text{CHMeS}(\text{O})\text{Et}$. The concentration ratio $[\text{Et}\cdot]:[\cdot\text{CHMeS}(\text{O})\text{Et}]$ was solvent dependent, and was

³ W. T. Dixon, R. O. C. Norman, and A. L. Buley, *J. Chem. Soc.*, 1964, 3625.

⁴ W. Demerau, G. Lassman, and K. Lohs, *Z. phys. Chem. (Leipzig)*, 1969, **9**, 343.

⁵ B. C. Gilbert, R. O. C. Norman, G. Placucci, and R. C. Sealy, *J.C.S. Perkin II*, 1975, 885.

⁶ B. C. Gilbert, R. O. C. Norman, and R. C. Sealy, *J.C.S. Perkin II*, 1975, 308.

⁷ B.-M. Bertilsson, B. Gustafsson, I. Kuhn, and K. Torssell, *Acta Chem. Scand.*, 1970, **24**, 3590.

4.0:1 in freon and 0.77:1 in di-t-butyl peroxide-t-butyl alcohol (3:2 by volume) at 230 K.

Irradiation of di-isopropyl or di-t-butyl sulphoxide without peroxide in ethylene oxide-cyclopropane as solvent at 143 K gave rise to e.s.r. spectra assigned to the 1-methylethanesulphinyl radical¹⁰ [$a(\text{H})$ 9.90 G, g 2.010 8] or to the 1,1-dimethylethanesulphinyl radical¹¹ [singlet, g 2.010 8], respectively. No isopropyl or t-butyl radicals were detected, and it appears that the efficiency of photochemical C-S cleavage may decrease with the size of the alkyl groups in a dialkyl sulphoxide, whilst the persistence¹¹ and ease of detection¹⁰ of the alkanesulphinyl radicals increase. In the presence of di-t-butyl peroxide, Pr_i^2SO in freon gave rise to an intense spectrum of the isopropyl radical and a signal assigned⁹ to $\cdot\text{CMe}_2\text{S}(\text{O})\text{Pr}^i$; the relative concentration of the latter radical increased when t-butyl alcohol was added. Weak spectra of the t-butyl radical and the 1,1-dimethylethanesulphinyl radical were obtained during photolysis of di-t-butyl peroxide in the presence of Bu^t_2SO . The radicals detected by e.s.r. spectroscopy during the reactions of photochemically generated t-butoxyl radicals with a range of acyclic and cyclic sulphoxides are listed in Table 1.

The cyclic sulphoxides $\text{CH}_2[\text{CH}_2]_n\text{SO}$ ($n = 2-4$) underwent ring opening and gave rise to the alkyl radicals $\cdot\text{CH}_2[\text{CH}_2]_n\text{S}(\text{O})\text{OBu}^t$, the spectra of which showed selective broadening of the $M_{1\beta} = 0$ components as the temperature was lowered, indicating out-of-phase modulation of the splittings from the β -hydrogen atoms.

Reactions with Trimethylsiloxy Radicals.—Similar experiments were conducted using bistrimethylsilyl peroxide as a photochemical source of trimethylsiloxy radicals.¹² For all the sulphoxides intense spectra of the alkyl radicals produced by siloxydealkylation were detected. Competitive abstraction of hydrogen from C-H groups adjacent to sulphur was less important than for the reactions involving t-butoxyl radicals.

In a solvent mixture of freon and dichloromethane, DMSO gave rise to a strong spectrum of the methyl radical [$\cdot\text{CD}_3$ from $(\text{CD}_3)_2\text{SO}$] and no signal from the dichloromethyl radical was detected. Again in contrast to the result with di-t-butyl peroxide, Bu_2^tSO yielded an intense spectrum of the t-butyl radical, and in addition, a signal assigned to the 1,1-dimethylethanesulphonyl radical,¹³ $\text{Bu}^t\dot{\text{S}}\text{O}_2$ [$a(\text{H})$ 2.12 G (9 H), g 2.005 0]. This sulphonyl radical is probably formed because of the presence of a small amount of water in the sulphoxide, which is extremely hygroscopic, and is probably derived from 1,1-dimethylethanesulphinic acid by hydrogen abstraction.¹³ The sulphinic acid could be formed by hydrolysis of $\text{Bu}^t\text{S}(\text{O})\text{OSiMe}_3$ or by hydroxydealkylation of the sulphoxide,^{2-4,6} the hydroxyl radicals coming from photolysis of Me_3SiOOH or H_2O_2 produced by hydrolysis of $\text{Me}_3\text{SiO}\cdot\text{OSiMe}_3$. The radicals detected during photolysis of bistrimethylsilyl

⁸ C. Lagercrantz, *J. Phys. Chem.*, 1971, **75**, 3466.

⁹ P. M. Carton, B. C. Gilbert, H. A. H. Laue, R. O. C. Norman, and R. C. Sealy, *J.C.S. Perkin II*, 1975, 1245.

¹⁰ B. C. Gilbert, C. M. Kirk, R. O. C. Norman, and H. A. H. Laue, *J.C.S. Perkin II*, 1977, 497.

¹¹ J. A. Howard and E. Furimsky, *Canad. J. Chem.*, 1974, **52**, 555.

¹² P. G. Cookson, A. G. Davies, N. A. Fazal, and B. P. Roberts, *J. Amer. Chem. Soc.*, 1976, **98**, 616.

¹³ A. G. Davies, B. P. Roberts, and B. R. Sanderson, *J.C.S. Perkin II*, 1973, 626.

peroxide in the presence of the dialkyl sulphoxides are listed in Table 2.

TABLE 1

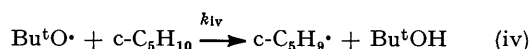
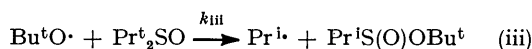
Radicals detected by e.s.r. spectroscopy during irradiation of di-*t*-butyl peroxide in the presence of dialkyl sulphoxides

| Sulphoxide ^a | Solvent ^b | Temp. (K) | Radicals detected ^c |
|--|----------------------|-----------|---|
| Me ₂ SO | F + A (1 : 1) | 218 | Me· (1), ·CH ₂ (Me)SO (2.0) ^{d,e} |
| Et ₂ SO | F | 230 | Et· (1), MeĈH(Et)SO (0.24) |
| Et ₂ SO | A + B (2 : 3) | 230 | Et· (1), MeĈH(Et)SO ^f (1.3) |
| Pr ⁱ ₂ SO | F | 220 | Pr ⁱ · (1), Me ₂ Ĉ(Pr ⁱ)SO ^g (ca. 0.1) |
| Pr ⁱ ₂ SO | F + A (1 : 1) | 220 | Pr ⁱ · (1), Me ₂ Ĉ(Pr ⁱ)SO ^g (0.56) |
| Pr ⁱ (Pr ⁿ)SO | F | 213 | Pr ⁱ · (1), Pr ⁿ · (0.09), Me ₂ Ĉ(Pr ⁿ)SO ^h (0.33) |
| Pr ⁱ (Et)SO | F | 213 | Pr ⁱ · (1), Et· (0.09), Me ₂ Ĉ(Et)SO ⁱ (0.25) |
| Bu ^t ₂ SO | F | 218 | Bu ^t ·, Bu ^t SO |
| Bu ^t (Me)SO | F | 213 | Bu ^t · |
| Bu ^t (CD ₃)SO | F | 213 | Bu ^t · ^j |
| Bu ^t (Et)SO | F | 218 | Bu ^t · ^j |
| Bu ^t (Pr ⁱ)SO | F | 218 | Bu ^t · ^j |
| Pe ^t (Pr ⁱ)SO | F | 218 | Pe ^t · (1), Pr ⁱ · (ca. 0.07) |
| $\overline{\text{CH}_2(\text{CH}_2)_4\text{SO}}$ | F + A (2 : 3) | 213 | Bu ^t OS(O)[CH ₂] ₄ ĈH ₂ ^k |
| $\overline{\text{CH}_2(\text{CH}_2)_3\text{SO}}$ | F + M (5 : 3) | 218 | Bu ^t OS(O)[CH ₂] ₃ ĈH ₂ ^l |
| $\overline{\text{CH}_2(\text{CH}_2)_2\text{SO}}$ | F | 198 | Bu ^t OS(O)[CH ₂] ₂ ĈH ₂ ^m |

^a Samples consisted of the sulphoxide (50–100 μl), di-*t*-butyl peroxide (100 μl), and solvent (500 μl); Pe^t = *t*-pentyl. ^b F = CCl₂FCF₂Cl, A = *t*-butyl alcohol, M = dichloromethane, B = di-*t*-butyl peroxide, C = cyclopropane. ^c Relative radical concentrations are given in parentheses. ^d *a* (2 H) 19.5 G, *g* 2.002 6. ^e ·CH₂CMe₂OH was also present. ^f *a* (2 H_α) 19.8, *a* (3 H_β) 25.0 G, *g* 2.002 6. ^g *a* (6 H) 22.4 G, *g* 2.002 6. ^h *a* (6 H) 22.5 G, *g* 2.002 6. ⁱ *a* (6 H) 22.5 G, *g* 2.002 6. ^j [Bu^t·]/[R·] ≥ 15 where R = CD₃, Et, or Prⁱ respectively. The spectrum of Bu^t· was intense in each case. ^k *a* (2 H_α) 22.0, *a* (2 H_β) 28.3, *a* (2 H_γ) 0.7 G. ^l *a* (2 H_α) 22.0, *a* (2 H_β) 28.4, *a* (2 H_γ) 0.7 G, *g* 2.002 6. ^m *a* (2 H_α) 22.0, *a* (2 H_β) 28.0, *a* (2 H_γ) 0.45 G, *g* 2.002 7.

Reactions with Ethoxyl Radicals.—In view of the possibility that the differences in reactivities of *t*-butoxyl and of trimethylsiloxy radicals were steric in origin, we briefly investigated the reaction of ethoxyl radicals with dialkyl sulphoxides. Irradiation of a mixture of diethyl peroxide and di-*t*-butyl sulphoxide at 218 K in freon as solvent gave rise to an extremely weak spectrum of the *t*-butyl radical in addition to other signals, also detected when the sulphoxide was absent, which appear to result indirectly from the reaction of ethoxyl radicals with diethyl peroxide. A similar experiment with isopropyl *n*-propyl sulphoxide yielded spectra of both displaced alkyl radicals and [Prⁱ·]/[Prⁿ·] was ca. 10 at 213 K. Thus it appears that ethoxyl and *t*-butoxyl radicals exhibit similar reactivity and selectivity towards dialkyl sulphoxides.

Determination of Relative Reactivities.—The rate of *t*-butoxydealkylation of di-isopropyl sulphoxide was measured relative to that for hydrogen abstraction from cyclopentane.¹⁴



Weighed mixtures of sulphoxide and cyclopentane (c-C₅H₁₀) were prepared and di-*t*-butyl peroxide and freon solvent were added by volume. The value of [Prⁱ·]/[c-C₅H₉·] was determined during photolysis as a function of temperature and, for simple alkyl radicals which are

TABLE 2

Radicals detected by e.s.r. spectroscopy during irradiation of bistrimethylsilyl peroxide in the presence of dialkyl sulphoxides

| Sulphoxide ^a | Solvent ^b | Temp. (K) | Radicals detected ^c |
|--|----------------------|-----------|---|
| Me ₂ SO | F + M (2 : 1) | 213 | Me· |
| (CD ₃) ₂ SO | F + M (2 : 1) | 213 | ·CD ₃ |
| Et ₂ SO | F | 230 | Et· (1), MeĈH(Et)SO (ca. 0.1) |
| Pr ⁱ ₂ SO | F | 230 | Pr ⁱ · ^d |
| Pr ⁱ (Pr ⁿ)SO | F | 213 | Pr ⁱ · (1), Pr ⁿ · (0.5) |
| Pr ⁱ (Et)SO | F | 230 | Pr ⁱ · (1), Et· (0.4), Me ₂ Ĉ(Et)SO (ca. 0.1) |
| Bu ^t ₂ SO | F | 218 | Bu ^t ·, Bu ^t SO ₂ |
| Bu ^t (Me)SO | F | 248 | Bu ^t ·, Bu ^t SO ₂ , MeSO ₂ ^e |
| Bu ^t (CD ₃)SO | F | 248 | Bu ^t ·, ^f Bu ^t SO ₂ , CD ₃ SO ₂ |
| Bu ^t (Et)SO | F | 213 | Bu ^t · (1), Et· (0.11) |
| Pe ^t (Pr ⁱ)SO | F | 233 | Pe ^t · (1), Pr ⁱ · (0.56) |
| $\overline{\text{CH}_2[\text{CH}_2]_4\text{SO}}$ | F | 218 | Me ₃ SiOS(O)(CH ₂) ₄ ĈH ₂ ^g |
| $\overline{\text{CH}_2[\text{CH}_2]_3\text{SO}}$ | M | 173 | Me ₃ SiOS(O)(CH ₂) ₃ ĈH ₂ ^h |
| $\overline{\text{CH}_2[\text{CH}_2]_2\text{SO}}$ | F | 191 | Me ₃ SiOS(O)(CH ₂) ₂ ĈH ₂ ⁱ |

^a Samples consisted of the sulphoxide (50–100 μl), bistrimethylsilyl peroxide (100 μl), and solvent (500 μl); Pe^t = *t*-pentyl. ^b F = CCl₂FCF₂Cl, M = dichloromethane. ^c Relative radical concentrations are given in parentheses. ^d [Prⁱ·]/[Me₂ĈS(O)Prⁱ] ≥ 12. ^e *a* (3 H) 0.58 G, *g* 2.005 2. ^f [Bu^t·]/[·CD₃] ≥ 15. ^g *a* (2 H_α) 22.0, *a* (2 H_β) 28.0, *a* (2 H_γ) 0.7 G. ^h *a* (2 H_α) 21.8, *a* (2 H_β) 28.3, *a* (2 H_γ) 0.7 G. ⁱ *a* (2 H_α) 22.0, *a* (2 H_β) 27.5, *a* (2 H_γ) 0.45 G, *g* 2.002 7.

destroyed by self- and cross-reactions at close to the diffusion-controlled limiting rate,^{14,15} it may be shown that equation (v) holds.

$$k_{\text{III}}/k_{\text{IV}} = [\text{Pr}^i\cdot][\text{c-C}_5\text{H}_{10}]/[\text{c-C}_5\text{H}_9\cdot][\text{Pr}^i_2\text{SO}] \quad (\text{v})$$

The results (Table 3) are averages of several runs for which [Prⁱ₂SO]/[c-C₅H₁₀] was varied over a factor of four. Similarly, the rate constants for *t*-butoxydealkylation of other dialkyl sulphoxides were determined by employing suitable competitors for the *t*-butoxyl radical. The results are given in Table 3, and in Table 4 are compared the relative rates of attack at sulphur in the sulphoxides and at hydrogen in cyclopentane. Absolute rate constants for *t*-butoxydealkylation, obtained by taking ¹⁴ log₁₀(*k*_{IV}/1 mol⁻¹ s⁻¹) = 9.0 – 21.8/θ where θ = 2.303RT kJ mol⁻¹, are also given in Table 4.

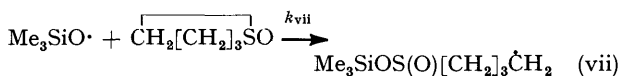
Trimethylsiloxy radicals proved much less selective than *t*-butoxyl radicals in intermolecular competition reactions. Photolysis of Me₃SiO·OSiMe₃ in the presence of a mixture of diethyl sulphoxide and tetramethylene sulphoxide showed that (*k*_{V1}/*k*_{VII}) was 0.46 at 233 K (*cf.* 0.030 for *t*-butoxydealkylation).

Reactions involving Alkyl Alkanesulphinates.—Irradiation of a mixture of methyl methanesulphinate [MeS(O)OMe]

¹⁴ A. G. Davies, D. Griller, and B. P. Roberts, *J. Chem. Soc. (B)*, 1971, 1823.

¹⁵ D. Griller and K. U. Ingold, *Internat. J. Chem. Kinetics*, 1974, **6**, 453.

and di-*t*-butyl peroxide in cyclopropane between 163 and 223 K gave rise initially to a strong spectrum of the methyl



radical, but a signal from the hydroxymethyl radical became apparent after a few minutes' irradiation and thereafter steadily grew in intensity. No spectrum which might

of di-*t*-butyl peroxide at 150 K the spectra of several carbon-centred radicals were apparent, including those of the methyl radical and of a species showing *a* (2 H_α), 22.0, *a* (2 H_β) 28.5, *a* (2 H_γ) 0.85 G, *g* 2.002 6, which we consider to be the 4-hydroxybutyl radical ($\cdot\text{CH}_2[\text{CH}_2]_3\text{OH}$). The same spectrum was obtained during irradiation of *n*-butyl *t*-butyl peroxide in cyclopropane, and this radical is probably derived by 1,5-hydrogen transfer in the *n*-butoxyl radical.¹⁶ In both experiments the photolysate was yellow (probably owing to the presence of Pr^{III}CO·COPr^{III}) and other signals, identical with those obtained

TABLE 3

Relative rates of sulphoxide *t*-butoxydealkylation in CCl₂FCF₂Cl as solvent

| Reagent A | Reagent B | Temp. range (K) | log ₁₀ (A _A /A _B) | E _A - E _B / kJ mol ⁻¹ | k _A /k _B at 233 K |
|--|--|-----------------|---|---|--|
| Pr ⁱ ₂ SO | <i>c</i> -C ₅ H ₁₀ | 213—253 | 0.0 ± 0.5 | -0.2 ± 0.2 | 1.11 ± 0.15 |
| $\overline{\text{CH}_2[\text{CH}_2]_3\text{SO}}$ | Pr ⁱ ₂ SO | 200—235 | -0.7 ± 0.4 | -9.0 ± 1.5 | 21.0 ± 2.0 |
| Et ₂ SO | $\overline{\text{CH}_2[\text{CH}_2]_3\text{SO}}$ | 228—243 | -0.3 ± 0.5 | 5.5 ± 2.0 | 0.030 ± 0.005 |
| Bu ^t (Me)SO | $\overline{\text{CH}_2[\text{CH}_2]_3\text{SO}}$ | 223—250 | 0.6 ± 0.2 | 0.8 ± 0.4 | 2.6 ± 0.2 |
| Bu ^t (CD ₃)SO | $\overline{\text{CH}_2[\text{CH}_2]_3\text{SO}}$ | 223—250 | 0.8 ± 0.3 | 1.5 ± 0.5 | 2.9 ± 0.2 |
| Bu ^t (Pr ⁱ)SO | $\overline{\text{CH}_2[\text{CH}_2]_3\text{SO}}$ | 212—251 | 0.3 ± 0.7 | 3.8 ± 2.0 | 0.30 ± 0.05 |
| $\overline{\text{CH}_2[\text{CH}_2]_2\text{SO}}$ | Bu ^t (Me)SO | 238—278 | 0.5 ± 0.2 | -2.3 ± 0.6 | 10.4 ± 1.0 |
| $\overline{\text{CH}_2[\text{CH}_2]_4\text{SO}}$ | Et ₂ SO | 220—258 | -0.4 ± 0.5 | -1.3 ± 0.6 | 0.8 ± 0.1 |
| Me ₂ SO ^a | Et ₂ SO ^a | 233 | | | ≤ 0.10 |
| Bu ^t ₂ SO ^a | Et ₂ SO ^a | 233 | | | ≤ 0.14 |

^a Indirect competition. A mixture containing a known weight of the sulphoxide (R₂SO), di-*t*-butyl peroxide, and a reproducible volume of ethylene oxide in cyclopropane diluent was made up using a vacuum line and irradiated at 233 K. [R·]/[$\overline{\text{OCH}_2\text{CH}\cdot}$] was estimated and, although only for Et₂SO was a measurable signal from R· detected, limits could be obtained for the relative reactivities of Me₂SO and Bu^t₂SO.

be attributed to the adduct $\cdot\text{SMe(O)(OMe)(OBu}^t)$ was observed. Photolysis of bistrimethylsilyl peroxide in the presence of MeS(O)OMe yielded an intense spectrum of

TABLE 4

Relative and absolute rate constants at 233 K and Arrhenius parameters for *t*-butoxydealkylation of dialkyl sulphoxides in CCl₂FCF₂Cl as solvent

| Sulphoxide | k _{rel} | log ₁₀ (A/ 1 mol ⁻¹ s ⁻¹) | E/ kJ mol ⁻¹ | k _{absolute} / 1 mol ⁻¹ s ⁻¹ |
|--|------------------|--|----------------------------|--|
| Cyclopentane | (1.0) | (9.0) | (21.8) | 1.3 × 10 ⁴ |
| Me ₂ SO | < 0.1 | | | < 1.3 × 10 ³ |
| Et ₂ SO | 0.63 | 8.0 | 18.1 | 8.2 × 10 ³ |
| Pr ⁱ ₂ SO | 1.1 | 9.0 | 21.6 | 1.4 × 10 ⁴ |
| Bu ^t ₂ SO | < 0.1 | | | < 1.3 × 10 ³ |
| Bu ^t (Me)SO | 54.6 | 8.9 | 13.4 | 7.1 × 10 ⁵ |
| Bu ^t (CD ₃)SO | 60.9 | 9.1 | 14.1 | 7.9 × 10 ⁵ |
| Bu ^t (Pr ⁱ)SO | 6.3 | 8.6 | 16.4 | 8.2 × 10 ⁴ |
| $\overline{\text{CH}_2[\text{CH}_2]_2\text{SO}}$ | 568 | 9.4 | 11.1 | 7.4 × 10 ⁶ |
| $\overline{\text{CH}_2[\text{CH}_2]_3\text{SO}}$ | 23.1 | 8.3 | 12.6 | 3.1 × 10 ⁵ |
| $\overline{\text{CH}_2[\text{CH}_2]_4\text{SO}}$ | 0.50 | 7.6 | 16.8 | 6.5 × 10 ³ |

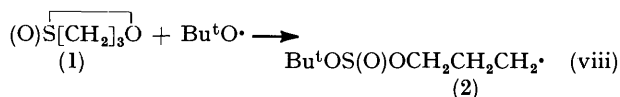
the methyl radical and a signal assigned to the methane-sulphonyl radical ¹³, * [a(3 H) 0.59 G, *g* 2.005 2]. Irradiation in the absence of peroxide produced no signals.

No spectrum was detected when *n*-butyl methanesulphinylate was irradiated alone in cyclopropane. In the presence

* This could arise by abstraction of hydrogen from MeS(O)OH, which might be produced by reaction of MeS(O)OMe with HO· (from H₂O₂ or Me₂SiOOH; see above), Me₃SiOOH, Me₃SiOH (from Me₃SiO·), or traces of water.

during irradiation of a mixture of di-*t*-butyl peroxide and butanal, indicated the intermediacy of *n*-propylcarbonyl radicals.

The cyclic sulphinate (1) underwent ring opening with *t*-butoxyl radicals to yield the alkyl radical (2) [*a* (2 H_α) 22.0, *a* (2 H_β) 28.5, *a* (2 H_γ) 0.7 G] in freon-CH₂Cl₂ at 173 K.



Although the signal from (2) was not strong, no spectrum which might be assigned to the adduct between *t*-butoxyl radicals and (1) was detected.

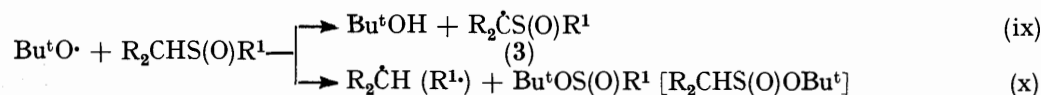
No signal which could be ascribed to $\cdot\text{SMe}_2(\text{O})\text{OMe}$ was detected during irradiation of azomethane in the presence of MeS(O)OMe; the only spectrum observed was that of the methyl radical.

DISCUSSION

t-Butoxydemethylation of DMSO is very much slower than hydroxydemethylation (*k ca.* 10⁸ l mol⁻¹ s⁻¹ at 233 K for a diffusion-controlled reaction in solvents of viscosities similar to that of freon), and this difference is probably not primarily due to a solvent effect (see below). Trimethylsiloxy radicals probably bring about homolytic substitution at sulphur much more readily than *t*-butoxyl radicals, although no absolute rate

¹⁶ J. K. Kochi in 'Free Radicals,' ed. J. K. Kochi, Wiley-Interscience, New York, 1973, vol. II, ch. 23.

constants are known for reactions of the siloxyl radicals. Consistent with this relative reactivity, $\text{Me}_3\text{SiO}\cdot$ is less selective than $\text{Bu}^t\text{O}\cdot$ in both intra- and inter-molecular oxydealkylation of sulphoxides.



Abstraction of hydrogen from a C-H group α to sulphur competes effectively with t-butoxydealkylation when the latter reaction is relatively slow [equations (ix) and (x), $\text{R} = \text{H}$ or Me], whereas hydrogen abstraction to form radicals of the type (3) was much less important with trimethylsiloxyl radicals.

The competition between reactions (ix) and (x) appears to be solvent-dependent, abstraction from the C-H group by t-butoxyl radicals becoming more important in the presence of t-butyl alcohol. It is difficult to interpret this solvent effect, but it may be ascribed tentatively to a reduction in the rate of t-butoxydealkylation due to the steric and electronic effects of hydrogen bonding of the alcohol to the S=O group of the sulphoxide.

Steric effects are clearly important in determining the rate of the overall displacement of alkyl radicals from sulphur. Thus, whilst the rate constant for t-butoxydealkylation increases along the series $\text{Me}_2\text{SO} < \text{Et}_2\text{SO} < \text{Pr}^i_2\text{SO}$, in line with the decreasing strength of the C-S bond, Bu^t_2SO is at least 11 times less reactive than Pr^i_2SO at 233 K. However, $\text{Bu}^t(\text{Me})\text{SO}$ undergoes dealkylation 50 times more rapidly than Pr^i_2SO to yield the t-butyl radical. Furthermore, $\text{Bu}^t(\text{Pr}^i)\text{SO}$ is *ca.* 9 times less reactive than $\text{Bu}^t(\text{Me})\text{SO}$ towards t-butoxyl radicals, the more stable t-butyl radical being displaced in both reactions.

In general, for an intramolecular competition between the two possible modes of cleavage of a mixed dialkyl sulphoxide, the more stable alkyl radical (primary < secondary < tertiary) is formed preferentially, but this selectivity is much lower for siloxy- than for t-butoxydealkylation. Irradiation of bistrimethylsilyl peroxide in the presence of DMSO or di-t-butyl sulphoxide gave rise to intense e.s.r. spectra of the displaced alkyl radicals, whereas t-butoxyl radicals reacted at rates sufficient to give only barely detectable signals. These differences in reactivity of $\text{Bu}^t\text{O}\cdot$ and $\text{Me}_3\text{SiO}\cdot$ are probably due to electronic rather than to steric effects, since $\text{EtO}\cdot$ appears to be no more reactive or less selective than $\text{Bu}^t\text{O}\cdot$.

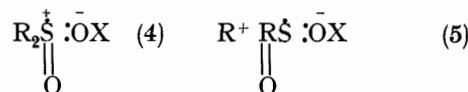
If the $\text{S}_{\text{H}2}$ reaction at sulphur is a concerted process, then the activation energies for hydroxy- or siloxy-

* The ionisation potentials, which may be used to measure orbital energies, of $\text{Bu}^t\text{O}\cdot$,^{18a} $\text{HO}\cdot$,^{18b} Me_2SO ,¹⁹ and Et_2SO ¹⁹ are *ca.* 9, 13.2, 9.0, and 8.8 eV, respectively. It seems reasonable to assume that the ionisation potential of $\text{Me}_3\text{SiO}\cdot$ is greater than that of $\text{Bu}^t\text{O}\cdot$ in view of the capacity of silicon to enter into $p\pi-d\pi$ -bonding involving a lone pair of electrons on oxygen.

¹⁷ I. Fleming, 'Frontier Orbitals and Organic Chemical Reactions,' Wiley-Interscience, New York, 1976, ch. 5.

dealkylation may be less than that for alkoxydealkylation because of polar effects. The greater electrophilicities of $\text{HO}\cdot$ and $\text{Me}_3\text{SiO}\cdot$ as compared with that of $\text{Bu}^t\text{O}\cdot$ would lead to increased contributions to the

transition state from canonical structures (4) and (5) when $\text{X} = \text{H}$ or Me_3Si .



Using frontier molecular orbital terminology,¹⁷ it is reasonable to assume that the initial interaction will involve the SOMO of $\text{XO}\cdot$ and the HOMO of R_2SO (essentially a non-bonding orbital centred on sulphur).* Thus the ease of electron transfer from the HOMO of the sulphoxide to the SOMO of $\text{XO}\cdot$ will be an important factor in determining the rate of dealkylation, which we would expect to decrease in the order $\text{XO}\cdot = \text{HO}\cdot$, $\text{Me}_3\text{SiO}\cdot > \text{Bu}^t\text{O}\cdot$, $\text{EtO}\cdot$.

There is an interesting parallel between the reactions of oxyl radicals with sulphoxides and with alkenes,²⁰ for which the interaction is also between the HOMO of the substrate and the SOMO of the radical. It has been shown²⁰ that the more electrophilic oxyl radicals, for example $\text{HO}\cdot$, $\text{Me}_3\text{SiO}\cdot$, and $\text{C}_4\text{F}_9\text{O}\cdot$, undergo predominant addition to propene, whereas t-butoxyl radicals abstract an allylic hydrogen in preference. Similarly, the values of $[\cdot\text{CHMeS(O)Et}]/[\text{Et}\cdot]$ during the reactions of $\text{Bu}^t\text{O}\cdot$, $\text{Me}_3\text{SiO}\cdot$, and $\text{HO}\cdot$ ⁶ with diethyl sulphoxide are 0.24, 0.05, and *ca.* 0, respectively. The absolute rate constant for addition of $\text{HO}\cdot$ to ethylene ($2.5 \times 10^9 \text{ l mol}^{-1} \text{ s}^{-1}$) is much larger than that for addition of $\text{MeO}\cdot$ ($3.7 \times 10^4 \text{ l mol}^{-1} \text{ s}^{-1}$) at 400 K.²¹

Although we have not succeeded in detecting an e.s.r. signal which might be assigned to an adduct of the type $\text{R}_2(\text{XO})\overset{\cdot}{\text{S}}\text{O}$, we consider it likely that a very short-lived intermediate is involved in oxydealkylation of sulphoxides. Morton and Preston²² have observed the e.s.r. spectrum of $\text{F}_3\overset{\cdot}{\text{S}}\text{O}$, produced by addition of photochemically generated fluorine atoms to F_2SO , which probably has the trigonal bipyramidal structure (6) analogous to that of the phosphoranyl radical $\cdot\text{PF}_4$.²³

¹⁸ (a) Taken as equal to the ionisation potential of the methoxyl radical: K. W. Egger and A. T. Cocks, *Helv. Chim. Acta*, 1973, **56**, 1516; (b) J. L. Franklin, J. G. Dillard, H. M. Rosenstock, J. T. Herron, K. Draxl, and F. H. Field, 'Ionization Potentials, Appearance Potentials, and Heats of Formation of Gaseous Positive Ions,' NSRDS-NBS 26, National Bureau of Standards, Washington, 1969.

¹⁹ H. Bock and B. Solouki, *Angew. Chem. Internat. Edn.*, 1972, **11**, 436.

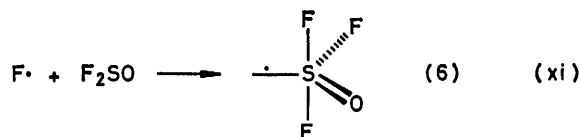
²⁰ M. P. Bertrand and J.-M. Surzur, *Tetrahedron Letters*, 1976, 3451.

²¹ E. A. Lissi, G. Massif, and A. Villa, *Internat. J. Chem. Kinetics*, 1975, **7**, 625.

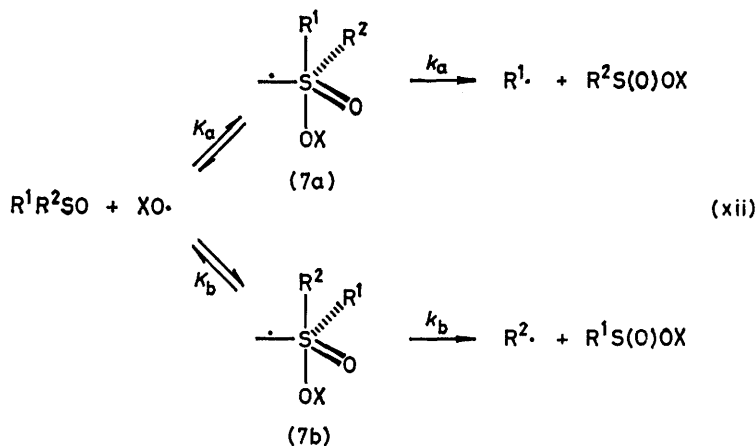
²² J. R. Morton and K. F. Preston, *J. Chem. Phys.*, 1973, **58**, 2657.

²³ R. W. Fessenden and R. H. Schuler, *J. Chem. Phys.*, 1966, **45**, 1845.

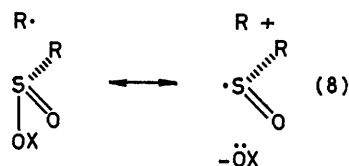
In terms of a two-step mechanism it is possible that both the rate of formation of the intermediate and the rate of its fragmentation to give alkyl radicals will be



greater for dealkylation by $\text{Me}_3\text{SiO}\cdot$ or $\text{HO}\cdot$ than by $\text{Bu}^t\text{O}\cdot$. More than one kinetic scheme can be envisaged; that given in equation (xii) is compatible with the observed results and appears attractive at present. The intermediates (7a and b) are considered to be in quasi-equilibrium with sulphoxide and oxyl radicals, and to fragment by cleavage of an apical, rather than an equatorial S-C bond.²⁴ It is unlikely that intramolecular exchange of R^1 and R^2 would occur prior to fragmentation of (7).^{24,*}



The higher electronegativities of Me_3SiO and HO as compared with RO groups should lead to a stabilisation of the four-co-ordinate intermediate relative to R_2SO and $\text{XO}\cdot$ (*cf.* the discussion of the stability of the transition state for a concerted reaction), and this could result in an increase in the overall rate constant for dealkylation ($k_{\text{overall}} = Kk$). An increase in the rate of dealkylation of the intermediate might result from stabilisation of the transition state for α -scission by a contribution from the polar structure (8) in which a negative charge



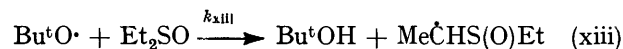
is carried by the oxyl ligand, and this stabilising effect should be more important for $\text{X} = \text{Me}_3\text{Si}$ or H than for $\text{X} = \text{Bu}^t$.

* The oxyl radical is assumed to enter into an apical site. The apicophilicities of the ligands in a sulphuranyloxyl radical are assumed to be in the order of group electronegativities, that is $\text{XO} > \text{R} > =\text{O}$, as is found for the related phosphoranyl radicals.²⁵

α -Scission could possibly be more exothermic for $\text{X} = \text{Me}_3\text{Si}$ or H than for $\text{X} = \text{Bu}^t$. The decreased intramolecular selectivity of siloxy- as compared with alkoxy-dealkylation could result from K_a/K_b and k_a/k_b [equation (xii)] both being closer to unity for the former reaction (Hammond postulate). For a given oxyl radical, the magnitude of K will be sensitive to the nature of R^1 and R^2 . The steric effect of increased α -branching of the alkyl groups will tend to decrease K ; however α -branching also leads to a decrease in ionisation potential of the sulphoxide¹⁹ which should favour formation of the intermediate. The magnitude of k should reflect the strength of the R-S bond which cleaves, and should increase in the order $\text{R} = \text{Me} < \text{Et} < \text{Pr}^i < \text{Bu}^t$. The above discussion is, of necessity, speculative, and it is possible that when R^1 or R^2 is a relatively stabilised radical (*e.g.* $\text{Bu}^t\cdot$) intermediate formation becomes rate-determining [*cf.* equation (xii)].

α -Sulphinylalkyl radicals, produced by abstraction of

hydrogen from a C_α -H group, were only detected when attack at sulphur in the dialkyl sulphoxide to bring about dealkylation was relatively slow. If it is assumed that the radical $\cdot\text{CHMeS(O)Et}$ is removed by self-reaction and reaction with the ethyl radical at close to the diffusion-controlled limiting rate, then it follows that k_{xiii} is *ca.* $2 \times 10^3 \text{ l mol}^{-1} \text{ s}^{-1}$ at 233 K, about 0.15 times the rate constant for abstraction of hydrogen from cyclopentane. This result is consistent with the previous



conclusion⁹ that there is little delocalisation of the unpaired electron onto the S=O substituent in an α -sulphinylalkyl radical.

t-Butoxyl radicals react with the cyclic sulphoxides

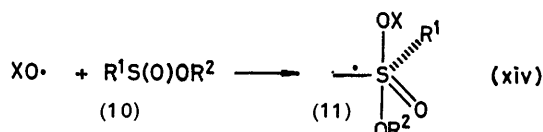


(9; $n = 2$ or 3) to bring about ring-opening more rapidly

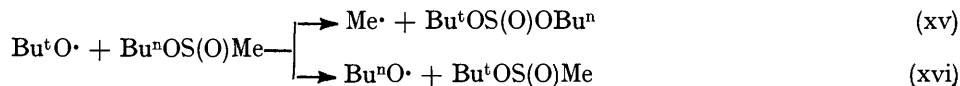
²⁴ J. W. Cooper, M. J. Parrott, and B. P. Roberts, *J.C.S. Perkin II*, 1977, 730.

²⁵ For analogies in phosphoranyl radical chemistry see J. W. Cooper and B. P. Roberts, *J.C.S. Perkin II*, 1976, 808.

than with (9; $n = 4$), which has about the same reactivity towards *t*-butoxydealkylation as diethyl sulph-



oxide. The relative reactivities of (9) ($n = 2 > 3 > 4$) may be interpreted in terms of relief of angle strain in



the four- and five-membered rings, but not in the six-membered ring, on forming the transition state or intermediate involved in dealkylation.*

The increase in steric compression of the groups around sulphur on going from the sulphoxide to the transition state or intermediate may be smaller for (9; $n = 2$ or 3) than for diethyl sulphoxide. For a two-step mechanism, it would in principle be possible for the rate constant for dealkylation of the intermediate to be greater or less than that for the acyclic analogue, diethyl sulphoxide. However, we were unable to detect the spectrum of an intermediate at low temperatures in reactions between (9) and *t*-butoxyl radicals.

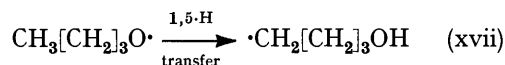
Reactions of Alkyl Alkanesulphinates.—In none of the reactions of dialkyl sulphoxides were we able to detect intermediate sulphuranyloxyl radicals by e.s.r. spectroscopy. By analogy with the established trends in phosphoranyl radical stability,^{24,25} we argued that the alkoxyl radical adducts of alkyl alkanesulphinates (10) might be more stable towards loss of an alkyl radical, since the less electronegative alkyl substituent would presumably occupy an equatorial site in the sulphuranyloxy-adduct (11).

Even at very low temperatures (≤ 153 K) no spectrum which could be ascribed to (11; $\text{X} = \text{Bu}^t$ or Me_3Si) was detectable from MeS(O)OMe . The spectrum of the methyl radical observed during the reaction of *t*-butoxyl radicals with MeS(O)OMe was much more intense than that obtained with DMSO, probably indicating that replacement of Me in DMSO by MeO increases the rate of $S_{\text{H}2}$ reaction at sulphur. This

could result from stabilisation of the transition state or intermediate involved in demethylation by the presence of a more electronegative ligand, an effect previously observed in *t*-butoxydealkylation of organotin compounds.²⁷

It appears that displacement of alkoxyl radicals from alkyl alkanesulphinates competes with dealkylation, since the 4-hydroxybutyl radical was detected during irradiation of di-*t*-butyl peroxide in the presence of

MeS(O)OBu^n . Alkoxyl radical addition to alkyl alkanesulphinates is thus readily reversible.



EXPERIMENTAL

E.s.r. spectra were recorded during continuous u.v. irradiation (Philips SP 500 A.C. water-cooled capillary mercury discharge lamp) of samples in the cavity of a Varian E-4 spectrometer. The apparatus and sample handling techniques have been described previously.^{25,28} Relative radical concentration measurements were made by electronic integration of suitable peaks followed by cutting out and weighing the derived absorption peaks from the recorder chart paper. g Factors were obtained by measurement of the microwave frequency (using a calibrated wavemeter) and the magnetic field at the centre of resonance, using a specially constructed proton magnetometer containing glycerol, the probe being placed alongside the cavity. The difference in magnetic field experienced by the probe and by the sample was small and was accounted for by determining the g factor of the pyrene radical anion (Na^+ counter ion) in tetrahydrofuran (g 2.002 710).²⁹ g Factors determined with this equipment are considered accurate to within ± 0.000 1.

Solvents which were liquids at room temperature were dried and distilled before use; cyclopropane (B.D.H.) and ethylene oxide (B.D.H.) were used as received. DMSO and $(\text{CD}_3)_2\text{SO}$ were obtained commercially. Other dialkyl sulphoxides were prepared by oxidation³⁰ with sodium periodate of the corresponding dialkyl sulphides, which were either commercially available or were prepared by standard methods;³¹ Bu^tSCD_3 was synthesised from CD_3I and Bu^tSH in alkaline solution.

Isopropyl n-propyl sulphoxide had b.p. 52 °C at 0.15 Torr (Found: C, 53.9; H, 10.6; S, 24.3. $\text{C}_6\text{H}_{14}\text{OS}$ requires C, 53.7; H, 10.5; S, 23.9%). *Isopropyl t-pentyl sulphoxide* had b.p. 62 °C at 0.1 Torr (Found: C, 60.1; H, 11.2; S, 20.0. $\text{C}_8\text{H}_{18}\text{OS}$ requires C, 59.2; H, 11.2; S, 19.8%).

Methyl³² and *n*-butyl³² methanesulphinates and the cyclic sulphinate (1)³³ were prepared by methods in the literature. Di-*t*-butyl peroxide was obtained commercially and purified before use; bistrimethylsilyl peroxide³⁴ and

* The strain energies of the related cyclic sulphides, $\text{CH}_2[\text{CH}_2]_n\text{S}$ ($n = 2, 3, \text{ or } 4$) are 82.4, 8.4, and -0.8 kJ mol⁻¹ respectively.²⁶

²⁶ J. D. Cox and G. Pilcher, 'Thermochemistry of Organic and Organometallic Compounds,' Academic Press, London, 1970, p. 574.

²⁷ A. G. Davies and J. C. Scaiano, *J.C.S. Perkin II*, 1973, 1777.

²⁸ R. W. Dennis, I. H. Elson, B. P. Roberts, and R. C. Dobbie, *J.C.S. Perkin II*, 1977, 889.

²⁹ B. G. Segal, M. Kaplan, and G. K. Fraenkel, *J. Chem. Phys.*, 1965, **43**, 4191; R. D. Allendoerfer, *J. Chem. Phys.*, 1971, **55**, 3615.

³⁰ C. R. Johnson and J. E. Keiser, *Org. Synth.*, 1966, **46**, 78.

³¹ D. T. McAllan, T. V. Cullum, R. A. Dean, and F. A. Fidler, *J. Amer. Chem. Soc.*, 1951, **73**, 3627.

³² I. B. Douglass, *J. Org. Chem.*, 1974, **39**, 563.

³³ N. K. Sharma, F. Jung, and T. Durst, *Tetrahedron Letters*, 1973, 2683; D. N. Harpp, J. G. Gleason, and D. K. Ash, *J. Org. Chem.*, 1971, **36**, 322.

³⁴ P. G. Cookson, A. G. Davies, and N. A. Fazal, *J. Organometallic Chem.*, 1975, **99**, C31.

n-butyl t-butyl peroxide³⁵ were prepared by published methods.

³⁵ P. G. Cookson, A. G. Davies, and B. P. Roberts, *J.C.S. Chem. Comm.*, 1976, 1022.

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