Configurational Selectivity in the Formation of the Trimethoxysulphuranyl Radical

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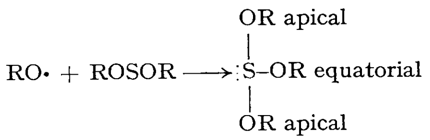
Summary Deuterium labelling experiments show that addition of MeO• to $(MeO)_2S$ to produce $(MeO)_3S$• is stereoselective such that the incoming radical takes up an apical site in the adduct.

We have recently reported the detection of the e.s.r. spectra of a series of trialkoxysulphuranyl radicals (I), produced in solution by the photolysis of dialkyl sulphoxylates [equations (1) and (2)].[1]

$$\mathrm{ROSOR} \longrightarrow \mathrm{RO}\cdot + \mathrm{ROS}\cdot \qquad (1)$$



$$\mathrm{RO}\cdot + \mathrm{ROSOR} \longrightarrow \overset{\text{OR apical}}{\underset{\text{OR apical}}{:\mathrm{S}\text{–OR equatorial}}} \qquad (2)$$

(I)

The spectrum of the trimethoxysulphuranyl radical (I; R = Me) exhibits hyperfine splitting from six equivalent protons [a(H), 1·7 G], and although no interaction with the protons of the equatorial methoxy-group was detected,[1] we have now confirmed the presence of this ligand by photolysis of $^{13}CH_3OSO^{13}CH_3$ which yields a spectrum showing a(H) 1·7 G (6H), a(^{13}C apical) 1·2 G (2C), and a(^{13}C equatorial) 5·8 G (1C) at 173 K in cyclopropane. Since apical and equatorial ligands give rise to different splittings it becomes possible to determine whether ligand exchange occurs during the lifetime of (I) and, if it does not, whether attack of the methoxyl radical on the sulphoxylate takes place in a stereoselective manner.

A cyclopropane solution containing dimethyl sulphoxylate (2 M) and triethyl phosphite† (0·5 M) was irradiated with u.v. light whilst in the cavity of an e.s.r. spectrometer, and the spectrum of the sulphuranyl radical (I; R = Me) was observed during continuous photolysis. Under similar conditions perdeuteriodimethyl sulphoxylate yielded the spectrum of (I; R = CD_3) [a(D), 0·3 G (6D) at 173 K].

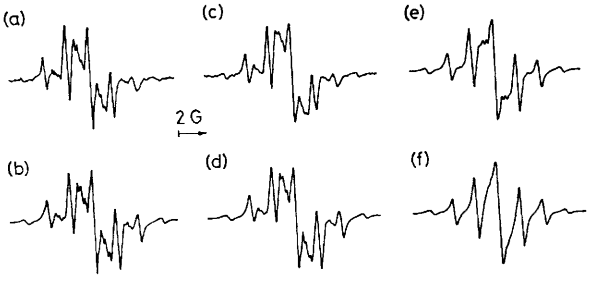


FIGURE. Experimental and simulated e.s.r. spectra of mixtures of $(CH_3O)_n(CD_3O)_{3-n}S\cdot$ (n = 0—3). (a) Sulphoxylate composition p = 0·25, q = 0·50, r = 0·25 at 163 K. (b) Computer simulation for A:B:C = 0·25:0·50:0·25. (c) Sulphoxylate composition p = 0·48, q = 0·00, r = 0·52 at 163 K. (d), (e), and (f) Computer simulations for A:B:C = 0·23:0·50:0·27, 0·31:0·33:0·35, and 0·48:0·00:0·52, respectively. For the computer simulations the hyperfine splittings from apical CH_3O and CD_3O groups were taken as 1·7 and 0·26 G, respectively, and the linewidth employed was the same for each type of radical.

An equimolar mixture of CH_3OH and CD_3OD was converted into the sulphoxylate,[1,2] which was shown by mass spectrometry to consist of a statistical mixture of $(CH_3O)_2S$, CH_3OSOCD_3, and $(CD_3O)_2S$ (mole fractions 0·25, 0·50, and 0·25 respectively). Photolysis of this mixture yielded a spectrum (see Figure a) which was shown by computer simulation to correspond closely to that predicted for a statistical mixture (type A:type B:type C = 0·25:0·50:0·25) of the three types of sulphuranyl radical which may be differentiated by e.s.r. spectroscopy. These radicals differ in the occupancy of their apical ligand sites; type A has two CH_3O groups, type B has one CH_3O and one CD_3O group, and type C has two CD_3O groups. This result implies that there are negligible isotope effects on the generation and reactions of methoxyl radicals and for the removal of sulphuranyl radicals from the system. The relative concentrations of types A, B, and C under continuous irradiation may thus be taken as proportional to their relative rates of formation.

The experiment was repeated using an approximately equimolar mixture of $(CH_3O)_2S$ and $(CD_3O)_2S$ (no CH_3OSOCD_3 was present‡) and the spectrum obtained (see Figure c) corresponds closely to that expected for A:B:C = 0·23:0·50:0·27. Intramolecular ligand exchange which occurs rapidly within the lifetime of (I) will lead to an A:B:C ratio given by $(p^2 + pr/3):(4pr/3):(r^2 + pr/3)$, where p and r are the mole fractions of $(CH_3O)_2S$ and $(CD_3O)_2S$, respectively. In this experiment p = 0·48 and r = 0·52, giving A:B:C = 0·31:0·33:0·35.

During these experiments the mole fraction (q) of CH_3OSOCD_3 is negligible and rapid intermolecular ligand exchange, of the types exemplified by reactions (3) and (4), will lead to the same sulphuranyl radical mixture as rapid intramolecular exchange.

$$(CH_3O)_3S\cdot + (CD_3O)_2S \longrightarrow (CH_3O)_2S + (CD_3O)_2CH_3OS\cdot \qquad (3)$$

$$(CH_3O)_2CD_3OS\cdot \xrightarrow{-CH_3OSOCD_3} CH_3O\cdot \xrightarrow{+(CD_3O)_2S} (CD_3O)_2CH_3OS\cdot \qquad (4)$$

We conclude that neither intra- nor inter-molecular ligand exchange takes place to an appreciable extent during the average lifetime of the sulphuranyl radicals. The ratio A:B:C will thus depend upon α, the fraction of reactive encounters between methoxyl radicals and dimethyl sulphoxylate molecules that lead to the attacking group taking up an apical site in the sulphuranyl radical. It may be shown that the ratio A:B:C for $q = 0$ is given by the relationship $p^2 + (1 - \alpha)pr : 2\alpha pr : r^2 + (1 - \alpha)pr$.

For p = 0·48 and r = 0·52 the ratio A:B:C is predicted to be 0·23:0·50:0·27 for $\alpha = 1$ (apical entry), 0·31:0·33:0·35 for $\alpha = 2/3$ (random entry), and 0·48:0·00:0·52 for $\alpha = 0$ (equatorial entry). Computer simulations of the spectra corresponding to these ratios are shown in the Figure. We conclude that the reaction of methoxyl radicals with dimethyl sulphoxylate occurs with a high degree of stereoselectivity, the incoming group taking up an apical site in the trimethoxysulphuranyl radical. Spectra in good agreement with those expected for apical entry were also obtained from sulphoxylate mixtures for which p = 0·66, r = 0·34 or p = 0·32, r = 0·68.

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† The phosphite is present to desulphurize the radical MeOS• [equation (1), ref. 1].

‡ Mass spectrometric studies showed that mixtures of $(CH_3O)_2S$ and $(CD_3O)_2S$ did not scramble in the presence of triethyl phosphite during u.v. irradiation under the conditions of the e.s.r. experiments. After detection of an e.s.r. spectrum (at 173 K) during photolysis of a cyclopentane solution containing $(CH_3O)_2S$ (1·83 M), $(CD_3O)_2S$ (1·94 M), and $(EtO)_3P$ (0.63 M), the mole fractions of the sulphoxylates were $(CH_3O)_2S$ 0·46, CH_3OSOCD_3, $\leqslant$0·012, and $(CD_3O)_2S$ 0·52.

Application of the principle of microscopic reversibility to reaction (2) implies that α-scission of the trimethoxysulphuranyl radical will involve cleavage of an apical S–O bond, although we do not yet have any measure of the rate of this fragmentation. It is usually assumed that radical attack on trivalent phosphorus[3] (as well as nucleophilic attack on four-co-ordinate phosphorus or three-co-ordinate sulphur)[4] involves apical entry to form the trigonal bipyramidal intermediate. Our demonstration that apical entry takes place in the formation of a sulphuranyl radical constitutes the first direct experimental evidence to justify such assumptions.

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