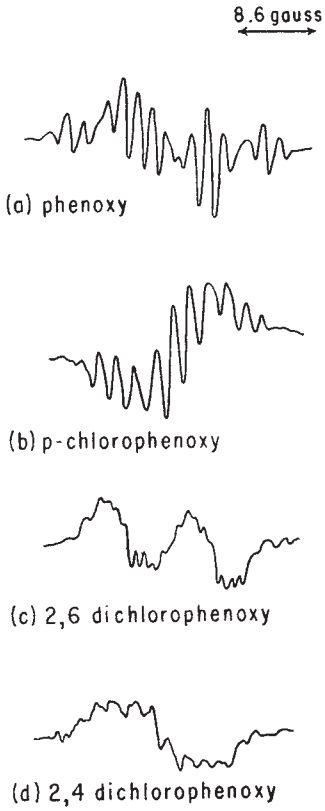

Fig. 1. Electron spin resonance spectra of (*a*) phenoxy, (*b*) *p*-chlorophenoxy, (*c*) 2,6-dichlorophenoxy, (*d*) 2,4-dichlorophenoxy radicals

the chlorine splittings. Comparing the splittings for phenoxy and *p*-chlorophenoxy radicals, we see that a doublet of 10·1 gauss and a triplet of 1·8 gauss in the phenoxy electron spin resonance spectrum are replaced by a sextet of 1·9 gauss in the *p*-chlorophenoxy radical spectrum. The sextet is due to an effective nucleus of spin quantum number 5/2, which it is reasonable to assume, to be made up of two equivalent protons (I = 1) and one equivalent chlorine nucleus (I = 3/2). This would mean that a chlorine in the 4 position of a phenoxy type radical produces a splitting of 1·9 gauss. A similar comparison with the electron spin resonance spectrum of 2,4-dichlorophenol shows the 4 position chlorine to give a splitting of 1·9 gauss. If we now made an assumption that the substituting of a Cl for an H does not change the distribution of the unpaired electron in the phenoxy radical drastically, we may make an estimate of the value of the ring chlorine splitting constant.

Using the equation[4]:

$$\Delta H_p = Q_p \rho$$

where ΔH_p is the splitting due to a ring proton, ρ is the unpaired electron density on the adjacent carbon atom, and Q_p is the ring proton splitting constant. We assume a similar relationship:

$$\Delta H_c = Q_c \rho$$

where Q_c is the ring chlorine coupling constant and ΔH_c the splitting it produces.

We may write then:

$$Q_c = Q_p \times \frac{\Delta H_c}{\Delta H_p}$$

$$Q_c = 0{\cdot}19\, Q_p$$

If we take Q_p to be 24·2 gauss[5], then:

$$Q_c = 4{\cdot}6 \text{ gauss} \pm 0{\cdot}6 \text{ gauss}$$

This value has been arrived at assuming there is no effect of the A on the π electron distribution.

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Chemiluminescent Reactions of SO with O and with O_3

The spectrum of the sulphur dioxide afterglow was first investigated in detail by Gaydon[1], who reported that it appeared to be continuous over its entire range from 2400 Å into the visible, apart from some weak bands above 3800 Å which are now known to arise from the (0,0,0) and (0,1,0) levels of the $^3B_1$ state of SO_2 (refs. 2 and 3). More recently, Herman *et al.*[4] have investigated the afterglow at low pressures and found no evidence of banded structure; they confirmed Gaydon's view that the afterglow was due to the chemiluminescent combination of O and SO, but did not establish whether it required a third body.

Recently, we have used a fast flow system to examine the reactions occurring in the products of a radiofrequency discharge through sulphur dioxide in an argon carrier, and have shown that the intensity (I) of the sulphur dioxide afterglow obeys the relation:

$$I = I_0[\text{O}][\text{SO}]$$

It has not, however, been possible to determine whether the quantity I_0 depends on total pressure. This alone might not establish that the luminescent reaction requires a third body since for the analogous air-afterglow reaction involving the chemiluminescent combination of O and NO to form electronically excited NO_2, the quantity I_0 is independent of pressure over a considerable range[5,6]. In this case, kinetic evidence[5] and the presence of banded structure near the high-frequency limit of emission[7] support the view that a third body is involved.

We have observed weak but definite banded structure near the short wave-length limit of the sulphur dioxide afterglow at room temperature. In separate experiments we have established that sulphur dioxide does not absorb significantly in this region until the product of concentration and path length is twenty times the maximum that could have been present in our experiments. This provides clear evidence that a third body is required for the chemiluminescent combination reaction O + SO and that the 'continuum' which reaches its maximum intensity at about 2700 Å is a mass of overlapping bands arising from many vibrational levels in the excited state.

The origin of the triplet bands is of interest. Gaydon[1] observed that they were more intense at higher pressures; in addition, we find that they are greatly enhanced when additional sulphur dioxide is added downstream from the discharge. This establishes that these bands are not due to long-lived triplet SO_2 formed in the discharge. The observation that this enhancement is not accompanied by any detectable shift in the overall spectral distribution from the ultra-violet to the visible suggests that the effect of added SO_2 is to increase the rate of vibrational relaxation in the triplet state of SO_2, since the appearance of the bands from the lowest vibrational levels would then be accompanied by a matching reduction in the intensity of that part of the 'continuum' which has a

maximum near 4500 Å (ref. 4) and which presumably consists of transitions from higher vibrational levels of the triplet state. This interpretation is supported by the observation that the triplet bands are enhanced, albeit to a lesser extent, by the addition to the discharge products of CO_2 or SF_6, both of which normally have high efficiencies for vibrational quenching. Molecular oxygen does not show this effect.

At relatively high pressures, oxygen atoms decay much more rapidly than SO, the reactions of which can then be examined readily beyond the point at which the sulphur dioxide afterglow has faded out. Under these conditions, added ozone undergoes a rapid reaction accompanied by blue and ultra-violet chemiluminescence. This reaction can only be:

$$SO + O_3 = SO_2 + O_2 + 106 \text{ kcal/mole} \qquad (1)$$

since the spectrum consists of strong emission from the $^3B_1$ state of SO_2 (minimum excitation energy 74 kcal/mole) and weaker emission from the $^1B_2$ state (threshold energy 85 kcal/mole). The emission from the $^3B_1$ state comes mainly from vibrational levels (0,0,0)and (0,1,0), although transitions from the (1,0,0) level appear weakly.

The $^1B_2$ emission is very different in distribution from the SO_2 afterglow. It consists of a series of bands commencing near 3000 Å which under low dispersion merge into a pseudo-continuum at about 3300 Å. This 'continuum' reaches its maximum at about 3500 Å and extends to 4000 Å. The bands observed cannot be due to self-reversal; they correspond to those which appear in absorption in this region. This is to be expected, since the highest frequency bands must be transitions to the lowest levels of the ground state. The highest energy band so far observed corresponds to (3,6,0), (4,3,0) or (5,0,0) in Metropolis's scheme[8], and it seems clear that the pseudo-continuum at longer wave-lengths arises from overlapping bands mainly involving lower vibrational levels of the excited state.

A strict proportionality was always observed between the intensities of the singlet and the triplet bands; we therefore conclude that both states are populated by the same reaction and that the $^1B_2$ state is not populated in the collision of two $^3B_1$ molecules by a mechanism analogous to that of delayed fluorescence[9].

There is a clear similarity between reaction (1) and the chemiluminescent reaction[10,11]:

$$NO + O_3 = NO_2 + O_2 + 48 \text{ kcal/mole} \qquad (2)$$

which has recently been shown to populate lower vibrational levels of the excited state of NO_2, which is also responsible for the air-afterglow emission[11].

Reaction (2) has been shown to have a higher activation energy when it yields electronically excited NO_2 than when ground state NO_2 is formed[11]. On this basis[12], reaction (1) would be expected to have successively higher activation energies to yield SO_2 in its ground ($^1A_1$), $^3B_1$ and $^1B_2$ states. This would explain why the $^3B_1$ emission is roughly ten times more intense than the $^1B_2$ emission in the $SO + O_3$ reaction, while the reverse is true in the O + SO reaction, which is expected to have zero activation energy. The latter situation would be predicted from the radiative lives, which the relative intensities of the absorption spectra show to be much greater for the $^3B_1$ state than for the $^1B_2$ state.

For this reason it is unlikely that the observed vibrational energy distribution of molecules in the $^3B_1$ state resembles that with which they are formed. The radiative lives of the $^1B_2$ state[13] and of the emitting state of NO_2 (ref. 14) are much shorter; the vibrational energy distribution of the emitting states is therefore probably similar to that with which the excited molecules are formed. This distribution of energy together with Franck–Condon factors will determine the spectral distribution of the emission. To judge by the corresponding absorption spectra, the Franck–Condon factors make a large contribution to the observed spread of the emission, but these factors are unlikely to vary greatly from level to level in the upper state. Thus the difference in energy between a particular vibrational level and the most probable transition from it should be almost constant for a given excited state. Table 1 shows that, for the same emitter, the difference between the most probable energies of emission is equal to the difference between the exothermicities of the reactions forming it. This suggests that the difference between the exothermicity of the reaction and the most probable excitation energy is roughly constant.

Table 1

Reaction	Exothermicity (kcal/mole at 298° K)	Wave-length of max. emission (Å)	Energy of max. emission (kcal/mole)
$O + NO \rightarrow NO_2^*$	73	6000	48
$O_3 + NO \rightarrow NO_2^*$	48	12,000	24
$O + SO \rightarrow SO_2^*$ ($^1B_2$)	131	2700	106
$O_3 + SO \rightarrow SO_2^*$ ($^1B_2$)	106	3500	82

The general similarities between the four chemiluminescent reactions discussed here, the similarity of Franck–Condon factors suggested by the constant difference between columns two and four in Table 1, and the closeness of the measured radiative lives[13,14] and of the integrated absorption coefficients all suggest that the main visible and near ultra-violet absorption spectrum of NO_2 is analogous to the $^1B_2$–$^1A_1$ transition of SO_2, that is, that it is a $^2B_2 \leftarrow {}^2A_1$ transition (presumably $2b_1 \leftarrow 1a_2$) (ref. 15). The formation of $^1B_2SO_2$ molecules in reaction (1) is clearly accompanied by anomalous vibrational excitation. Detailed investigations of this and reaction (2) are being carried out since the examination of vibrational excitation in reactions which yield electronically excited species has advantages over the method of infra-red chemiluminescence[16]. These include the wider choice of detectors and the shorter radiative lives of the species involved, which makes it possible to work at higher pressures.

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Structures of Polymyxin *B2* and Polymyxin *E1*

In a previous communication[1], from the analysis of a partial acid hydrolysate, the structure of polymyxin *E*1 was shown to be limited to two alternatives, the so-called 7α and 8γ formulæ. By applying the enzyme method of hydrolysis as devised by Suzuki *et al.* in their determ-