O+SO Recombination Emission at 3500°K

BY S. R. FLETCHER AND B. P. LEVITT

Dept. of Chemistry, Imperial College of Science and Technology, London, S.W.7

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The rate of radiative recombination of O and SO has been measured by heating SO₂ in the shock tube. The rate at 3500°K combined with room temperature data gives the radiative rate constant as $1.5 \times 10^8 (T/298)^{-1.0}$ mole⁻¹ cm³ sec⁻¹.

One objective in chemical kinetics is the measurement of rate constants over a wide range of temperature. This paper describes the radiative recombination of SO+O at $3500^{\circ}K$.

When SO_2 is dissociated by an electrical discharge at room temperature, a glow is observed due to the reactions^{1, 2}:

$$SO + O + M \xrightarrow{1} SO_2^* + M$$
$$SO_2^* + M \xrightarrow{2} SO_2 + M$$
$$SO_2^* \xrightarrow{3} SO_2 + hv$$

SO₂^{*} denotes three excited electronic states of SO₂. Provided that $k_2[M] \ge k_3$, the intensity I of light emitted is given by $I = I_{oa}[SO][O]$ photons sec⁻¹cm⁻³ where $I_{oa} = k_1 k_3 / k_2$; I_{oa} is the radiative rate constant for the "reaction"

$$O + SO = SO_2 + hv.$$

Similar kinetics are observed for the air afterglow where SO, SO₂ in steps (1)-(3) are replaced by NO, NO₂.³ The value of I_{oa} and the spectral distribution for the air after-glow have been determined at room temperature by discharge flow experiments^{3, 4} and at 3750°K by experiments on shock-heated air.⁵ In the latter case, the overall emissivity has two distinct contributions from excited electronic states of NO₂: thermal emission, where NO^{*}₂ is formed by collisional excitation of NO₂, and after-glow, where NO^{*}₂ is formed from O+NO.⁶ The temperature dependence of the air afterglow has also been determined using glow-discharge shock-tube techniques.⁷

When SO_2 is heated in the shock tube, three excited electronic states are populated by collisions; thermal emission occurs at wavelengths betweeen 250 nm and 550 nm. The intensity observed rises to a peak behind the shock front; it then decays as the SO_2 dissociates and the gas cools. In earlier work⁸ at wavelengths between 250 and 260 nm the initial peak was superposed on a second contribution which rose from zero behind the front to a steady level; this was tentatively attributed to the O+SO recombination. At longer wavelengths the thermal emission was so intense that the recombination was masked. We now report measurements at higher temperatures : here SO_2 is nearly completely dissociated at equilibrium so the thermal emission is small.

S. R. FLETCHER AND B. P. LEVITT EXPERIMENTAL

Mixtures of SO₂ and Ar at a few mm total pressure were heated, compressed and set into motion by an incident shock wave. The light emitted by the hot gas passed through a quartz window in the side of the shock tube into a monochromator; the intensity was measured by a photomultiplier whose output was recorded by photographing a single sweep of an oscilloscope. Details of the apparatus, of the preparation of the gases, and of the calibration of the optical system have been described.⁸ For this work the sensitivity at 280 nm was redetermined using the thermal emission from SO₂: the oscilloscope deflection due to the thermal emission immediately behind the shock front was measured for a few runs with temperatures near 3800°K; these were compared to absolute intensity values obtained before.

Over a limited temperature range, the intensity of thermal emission is given by

$$I = I_{ot}[SO_2]_2 \exp(-E_a/RT)$$

where I_{ot} is independent of the other variables, E_a is a mean activation energy, and the subscript 2 denotes shocked gas. If I_{ft} is the thermal emission observed immediately behind the shock front, the thermal emission at chemical equilibrium is given by

$$I_{\rm et} = I_{\rm ft}([{\rm SO}_2]_{\rm e}/[{\rm SO}_2]_{\rm f}) \exp(-E_a/R)(1/T_{\rm e}-1/T_{\rm f})$$
(1)

where $[SO_2]_f$ and $[SO_2]_e$ are the concentrations of SO_2 and T_f and T_e are the temperatures at the front and at equilibrium.

Shocked gas conditions were calculated from the measured shock velocity D: all molecules were assumed to be vibrationally and rotationally relaxed in times short compared to the time of measurement. The composition of the shocked gas at partial and complete chemical equilibrium was calculated using the University of California Los Alamos Scientific Laboratories HUG computer programme.⁹ Partial chemical equilibrium corresponded to chemical equilibrium amongst the restricted list of molecules SO₂, Ar, SO, O, O₂ and SO₃. The latter and other possible sulphur oxides were always present in negligible proportions. For full equilibrium S and S₂ were included; the concentration of sulphur molecules with more than two atoms was also negligible.

Another possible partial equilibrium state includes S but not S_2 in the list of products, due to the nearly thermoneutral steps $O+SO \rightarrow S+O_2$. However, the values of [O] and [SO] calculated for this state do not differ appreciably from those calculated for complete equilibrium, so that it need not be considered separately.

RESULTS

Fig. 1 shows some oscilloscope traces. The first was obtained at an equilibrium temperature of about 3200°K. The intensity reaches at least 80 % of its final steady level within roughly twice the time required for the thermal emission peak to decay by 50 %. At lower temperatures dissociation was not complete within half the available observation time, and equilibrium measurements were not possible. For stronger shocks where T_e exceeded about 3600°K the intensity declined behind the front, but then increased for the rest of the time of observation. At still higher temperatures where T_e was about 4500°K, the intensity again became nearly constant after the thermal emission had decayed, but at a much higher level than the runs at lower temperatures.

For all runs the observed equilibrium intensity was corrected for the contribution due to thermal emission :

$$I_{\rm e} = I_{\rm e}({\rm obs.}) - I_{\rm et}.$$

 $I_{\rm et}$ was usually about 2 % of the observed equilibrium intensity and was never more than 10 %. For reasons discussed below quantitative observations were confined to partial equilibrium temperatures below 3700°K. Some runs below this temperature

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showed a slow increase in intensity with time after the initial decay. In these cases, I_e was measured after about twice the time required for the decay of the initial peak; except for a few runs noted below, I_e at this point did not differ from the final intensity by more than 20%.



VARIATION OF INTENSITY WITH WAVELENGTH

The spectral distribution of the emission is shown in fig. 2. At each wavelength the value of I_e was measured for a few runs at shock velocities around 2.25 mm μ sec⁻¹. The mixture used had a mole fraction m of SO₂ of 0.05 at total initial pressure



FIG. 2.—Points: intensity of equilibrium emission (photons, arbitrary units) against wavelength.

 $p_1 = 5$ mm. Calculated shocked gas conditions for this mixture and shock strength are: $T_f = 4650^{\circ}$ K; at partial equilibrium $T_e = 3630^{\circ}$ K, pressure = 0.46 atm, $\rho_2/\rho_1 = 5.46$, $[SO_2] = 3.8 \times 10^{-9}$, $[Ar] = 1.39 \times 10^{-6}$, $[SO] = 7.0 \times 10^{-8}$, $[O] = 6.4 \times 10^{-8}$, $[O_2] = 2.7 \times 10^{-9}$, all in mole cm⁻³. At full equilibrium, $T_e = 3390^{\circ}$ K,

pressure = 0.46 atm, $\rho_2/\rho_1 = 5.88$, [SO₂] = 8.8×10^{-9} , [Ar] = 1.50×10^{-6} , [SO] = 3.8×10^{-8} , [O] = 7.7×10^{-8} , [O₂] = 1.3×10^{-8} , [S] = 3.1×10^{-8} , [S₂] = 4.3×10^{-8} .

 I_e did not vary systematically with shock velocity so the values at each wavelength were averaged to give the points in fig. 1; a total of 32 runs were made at 12 wavelengths. The measurements were limited at low wavelengths by inadequate signal-to-noise ratio; at the highest wavelengths the intensities became less reproducible and further measurements would be desirable.

The spectral distribution for the O+SO glow at room temperature² and for the thermal emission at 3333°K⁸ are shown in fig. 2. They are scaled so their maxima have the same value as the experimental curve. The equilibrium emission follows the O+SO room temperature distribution at wavelengths above 280 nm, but falls off more rapidly at shorter wavelengths.

VARIATION OF INTENSITY WITH TEMPERATURE AND COMPOSITION

The absolute intensity of the emission was measured at 280 nm for runs with m = 0.05, $p_1 = 5$ and 10 mm, and at m = 0.10, $p_1 = 5$ mm. The spectral intensity at 280 nm was converted to an absolute total intensity by integrating the dashed curve in fig. 2. The dashed curve was assumed to have the same shape as the O+SO spectral distribution at room temperature at wavelengths above 340 nm. The total



FIG. 3.—A logarithm of I_{0a} against reciprocal temperature. Squares, $p_1 = 5$ mm, m = 0.05; open circles, 10 mm, 0.05; filled circles, 5 mm, 0.10; curve, see text.

intensity in photons sec⁻¹ cm⁻³ was divided by the partial equilibrium product [O][SO] to give the radiative rate constant I_{oa} . Since $k_2[M] \gg k_3$ at 1 mm or less at 298°K,² the inequality will certainly be satisfied under our conditions where [M] is at least ten times greater.

 I_{oa} is shown plotted against the partial equilibrium temperature in fig. 3. The values show no systematic temperature dependence. A plot of I_{oa} using full equilibrium values is similar to fig. 3, but shifted to higher values because the [O][SO] product is smaller.

Some of the m = 0.05, 5 mm runs in fig. 3 showed equilibrium intensities which increased more rapidly with time than the limit set above. Although values of I_{oa} from these runs are in line with the rest, runs with this mixture have not been used to determine I_{oa} . The other points as a group give a mean value $I_{oa} = 7.0 \times 10^{30}$ photons sec⁻¹ mole⁻² cm³, or 1.2×10^7 mole⁻¹ cm³ sec⁻¹. The standard deviation of the

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16 points is 0.08 \log_{10} units, a scatter of 20 % about the mean value. If full equilibrium is assumed the value of I_{oa} is 40 % higher at 1.6×10^7 mole⁻¹ cm³ sec⁻¹, with a scatter of 15 % about the mean.

Returning to the partial equilibrium assumption, the ratio of the highest to the lowest value of I_{oa} plotted is 1.8:1. The ratio of the highest to the lowest value of the [O][SO] product for these runs was 7.8:1. The scaling is thus reasonably good. However, the mean of the 10 mm, m = 0.05 runs is 36 % higher than the mean of the 5 mm, m = 0.10 runs; for full equilibrium the means differ by 26 %. These differences are statistically significant.

DISCUSSION

The equilibrium emission observed is not due to thermal emission from SO_2 since it is between one and two orders of magnitude too large. Substantial contributions from other sources can be excluded by considering the temperature dependence of the intensity. I_e increases by a factor of 4.8 from 3050 to 3450°K corresponding to an apparent activation energy E_a of 360 kJ. However, $I_e/[O][SO]$ shows only a small temperature variation, as expected for chemiluminescence. If the emission were due to S+S two or three body recombination or to O+S chemiluminescence, the quantities $I_e/[S]^2$ and $I_e/[O][S]$ should have low values of E_a ; in fact, these are -300 kJ and -265 kJ respectively, values inconsistent with these processes. For thermal emission from a molecule, the value of E_a should not be lower than the photon energy by more than about 100 kJ,^{6,8} setting a lower limit of 325 kJ at 280 nm. E_a for $I/[S_2]$ is only 100 kJ, so thermal emission from S_2 is unimportant. For I/[SO], E_a is 270 kJ so thermal emission from SO is not excluded by this argument. However, the broad emission spectrum observed is unlikely for a diatomic molecule. Since the observed emission shows a spectral distribution similar to that observed for O + SO at room temperature and since it scales satisfactorily with concentration and temperature, it seems reasonable to identify it with O+SO recombination emission.

 ΔH_{298}° for O+SO = SO₂ is -544 kJ.² A molecule of SO₂ which has just been formed by the recombination of O+SO will thus have $544 - E_0$ kJ of vibrational energy: E_0 is the difference in energy between the lowest levels of the upper state and those of the ground state. At room temperature, vibrational relaxation is slow compared to quenching, so most molecules radiate or are quenched in the vibrational levels in which they are formed. The shortest wavelength observed at room temperature, 220 nm, corresponds to an energy of 544 kJ, which is the maximum available.² However, at 3500°K vibrational relaxation will be much faster, and newly formed SO₂^{*} molecules may well lose vibrational energy before radiating. The intensity at shorter wavelengths from molecules with excess vibrational energy will thus be reduced, as observed experimentally.

At high temperatures the emission was observed to increase continuously with time; this may be due to the formation of S_2 which emits throughout the visible.¹⁰ At the highest temperatures the intensity reaches a steady level after the initial thermal peak, but the level was much higher than those at lower shock strengths. This is probably due to thermal emission from S_2 and SO.

 I_{oa} for the 10 mm, m = 0.05 runs is higher than for the 5 mm, m = 0.10 runs. This is not due to chance. The points for the more dilute mixture are at lower temperatures; the curve in fig. 3 represents the temperature dependence of I_{oa} (see below), and this is insufficient to account for the difference in the mean values of I_{oa} . The difference may be partly due to flow effects. Also if we take into account the different molecules M present in steps (1) and (2), $I_{oa} = k_3 \Sigma k_{1,i} [M_i] / \Sigma k_{2,i} [M_i]$.

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(2) now includes all collisional steps which remove SO_2^* . Thrush² has shown that SO_2 is three times as effective as argon in quenching the ¹B and ³B states of SO₂, but is only moderately more efficient as a third body in (1). I_{oa} will thus fall as the proportion of SO_2 present is increased. In addition, at these temperatures the exothermic step $SO_2^* + SO_2 \rightarrow SO + SO_3$ may also be effective; the analogue $NO_2^* + NO_2 \rightarrow$ $NO + NO_3$ goes on at least one collision in 4 at 2000°K.⁶ At partial equilibrium the main constituents other than argon are O, SO and O₂, but these may also be more effective than argon in quenching and chemical quenching steps. The value of I_{oa} for a very dilute mixture where M is argon is probably slightly higher than the observed value for the 5 and 10 % mixtures. The experimental results are not accurate enough to justify further analysis of the variation of I_{oa} with m. Since we cannot be certain whether partial or full equilibrium is attained our best estimate at 3500°K is the mean value $1.4\pm0.4\times10^7$ mole⁻¹ cm³ sec⁻¹; the corresponding value at room temperature is 1.5×10^8 mole⁻¹ cm³ sec⁻¹.² The radiative rate constant thus shows a slight negative temperature dependence : $I_{oa} = 1.5 \times 10^8 (T/298)^{-1.0}$ mole⁻¹ cm³sec⁻¹. The value of the exponent -1.0 is lower than that for the air afterglow which was found to be -2.1 and -1.6 in ref. (6) and (7) respectively. These negative temperature dependences for the radiative rate constants reflect the negative temperature dependence of the termolecular recombination step (1).

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