

## FORMATION OF EXCITED BrCl ( $B^3\Pi(0^+)$ ) IN THE REACTION OF BROMINE WITH CHLORINE DIOXIDE

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### Summary

The reaction of Br<sub>2</sub> with OClO is a self-propagating chain reaction which emits red and near infrared chemiluminescence ( $\lambda > 600$  nm) owing to the  $B^3\Pi(0^+)-X^1\Sigma^+$  transition of BrCl. The rate-controlling step



is followed by reactions of BrO and ClO radicals that propagate the chain. Based on the steady state vibrational distribution determined for the B-X band system, electronically excited BrCl\* (B) is believed to be formed in the reaction



The overall photon yield  $\Phi$  of BrCl chemiluminescence from the Br<sub>2</sub> + OClO reaction was found to exceed  $3 \times 10^{-3}$ . Typical steady state BrCl\* concentrations were about  $3 \times 10^7$  molecule cm<sup>-3</sup> using  $[\text{OClO}]_0 = [\text{Br}_2]_0 = 2.3 \times 10^{13}$  molecule cm<sup>-3</sup>.

A partial rotational analysis of the B-X spectrum of BrCl has resulted in new spectroscopic constants for the ground and excited states of <sup>81</sup>Br<sup>35</sup>Cl and of <sup>79</sup>Br<sup>35</sup>Cl.

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### 1. Introduction

Recently, a high power continuous working iodine atom laser operating on the <sup>2</sup>P<sub>1/2</sub>-<sup>2</sup>P<sub>3/2</sub> electronic transition near 1.3 μm has been successfully

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demonstrated [1] using chemical pumping by collisions with singlet oxygen  $O_2^1\Delta_g$ . Optical pumping to lasing of the  $B^3\Pi(O_u^+)-X^1\Sigma_g^+$  transitions of  $I_2$  and  $Br_2$  also has been shown [2, 3]. These results indicate the promising nature of certain electronic transitions for forming practical chemically pumped lasers, such as the B-X transition of BrCl.

A fundamental limitation of the possibilities for chemically pumped lasers is provided by the rarity of chemiluminescent reactions, and of course also by the difficulty of ensuring a population inversion. The rapid reactions of metal atoms with oxidizers, *e.g.*, forming diatomic electronically excited oxides such as SmO, form a large class of chemiluminescent processes [4]. Most studies of these reactions have been carried out at low pressures approaching single-collision conditions [5]. Severe problems may be expected in scaling such chemiluminescent reactions up to higher pressures which are needed for the operation of a useful laser.

Clyne and Coxon [6] have shown that the reaction of atomic or molecular bromine with chlorine dioxide OClO gives rise to red and near IR chemiluminescence in the torr pressure range. The  $Br_2 + OClO$  reaction, once initiated by a Tesla discharge, is a self-propagating chain reaction and the chemiluminescence was found [6] to consist of vibrational bands of the  $B^3\Pi(O^+)-X^1\Sigma^+$  transition of BrCl. Clyne and Coxon [6] analysed bands from 600 to 950 nm, whilst Hadley *et al.* [7] later extended the analysis further into the IR to 1.15  $\mu m$ . Hadley *et al.* [7] modified some of Clyne and Coxon's vibrational assignments [6] at the longer wavelengths. These modifications have been confirmed by Clyne and Smith [8] who studied the kinetics of BrCl (B-X) emission produced by the radiative recombination of ground state  $Br^2P_{3/2} + Cl^2P_{3/2}$  atoms in the presence of a third body.

The chemiluminescent emission arises mainly from the lowest vibrational levels of the B state of BrCl and the most favoured Franck-Condon transitions are those involving high  $v''$ , such as the 0-15 and 1-12 bands. This result is illustrated by the potential energy curves of BrCl shown in Fig. 1 of ref. 9 and in Fig. 2(b) of ref. 8. Quantitative Franck-Condon factors are available from the work of Coxon [10] who studied the B-X band system in absorption at high resolution. Thus, the possibilities for forming an inversion on transitions such as the 0-15 band are clear, in the light of the low Boltzmann population of states such as  $v'' = 15$  at 300 K.

The nature of the elementary step forming excited BrCl in the  $Br_2 + OClO$  reactions has remained uncertain. However, a mass spectrometric kinetic study of ground state species involved in the  $Br + OClO$  reaction has been reported by Clyne and Watson [11]. They showed that the primary rate-controlling process in this reaction was the slightly endoergic step



with  $k_1 = 4.2 \times 10^{-13}$  and  $k_{-1} = 6.7 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K. ClO and BrO radicals were reaction intermediates [11], with BrCl as the major final product.

Studies of the kinetics of excited BrCl (B) in resolved quantum states have been reported by Clyne and McDermid [12]. They reported a radiative lifetime  $\tau_R = 40 \mu\text{s}$  for BrCl(B). Clyne and McDermid [12] and Wright *et al.* [13] found that electronic quenching of BrCl(B) by ground state Cl<sub>2</sub> or BrCl is very inefficient, with approximate efficiencies of  $5 \times 10^{-3}$  and  $1 \times 10^{-3}$  for quenching collisions with BrCl and Cl<sub>2</sub>. In contrast, vibrational relaxation (V-V transfer) within the B state manifold occurs at every collision of BrCl(B) with Cl<sub>2</sub> [12].

We now describe a new spectroscopic and kinetic study of BrCl emission from the Br<sub>2</sub> + OClO reaction. In the first part of the work the spectrum of the B-X chemiluminescence has been analysed with partial rotational resolution for the first time. In this way, it has been possible to isolate particular vibrational bands, as well as to obtain directly the first spectroscopic constants for the levels  $v' = 0$  and 1 and  $v'' = 10, 11$  and 12. Steady state vibrational populations were determined; these were non-Boltzmann and they suggest that the exoergic elementary step



is responsible for forming electronically excited BrCl(B). Estimates of the overall photon yield  $\Phi$  in the Br<sub>2</sub> + OClO reaction were made and the lower limit value for  $\Phi$  was  $3 \times 10^{-3}$ .

## 2. Experimental

A cylindrical reaction vessel (20 cm long  $\times$  3.0 cm i.d.) with cemented quartz windows was connected to a vacuum system. The upstream window was adjacent to the entrance slit of a 1 m Czerny-Turner monochromator which was equipped with a grating of 1200 lines  $\text{mm}^{-1}$  blazed at  $1.0 \mu\text{m}$  in first order and which gave a reciprocal dispersion of  $0.8 \text{ nm mm}^{-1}$ . For the higher resolution work, slit widths of  $25 \mu\text{m}$  were used with a scan speed of  $50 \text{ pm min}^{-1}$  in first order, in order to integrate sufficient photon counts. Full width at half maximum resolution under these conditions was  $50 \text{ pm}$ . The monochromator wavelength was calibrated with neon and mercury lines and some non-uniformity in the sine-bar drive was found and corrected for. The exit slit carried a GaAs photomultiplier (RCA C31034) usually operated at 195 K and at 1250 V. Detected photoelectrons were input to an amplifier-discriminator (SSRI 1120), a ratemeter and a Y-T recorder. The background count rate (dark + noise) was usually about  $1 \text{ s}^{-1}$ .

To measure relative band intensities, another photomultiplier (E.M.I. 9789QB) was placed at the downstream window of the reaction cell to measure relative integrated intensities. As the OClO flow slowly depleted during a scan, the measured integrated intensities were used to correct the resolved intensities for reduction in intensity due to the fall in OClO concentration.

The quantum efficiency of the C31034 photomultiplier, as a function of wavelength, was taken from the manufacturer's tables. However, at the longer wavelengths investigated (about 854 nm) the sensitivity was less than expected when this photomultiplier was operated at 195 K. Operation at 273 K improved the sensitivity to the 0–12 band at 854 nm by a factor of 2.0, whereas sensitivity to the 1–12 band (maximum intensity near 839.1 nm) was practically unaffected by temperature.

For measurements of the photon yield of the  $\text{Br}_2 + \text{OCIO}$  reaction, the monochromator was removed and the C31034 detector was used to measure integrated intensity. The actinometer system was the chemiluminescent reaction between ozone and nitric oxide [14, 15]. Ozone concentrations were measured using absorption along the length of the reaction vessel, with a deuterium lamp as the source and two 254 nm interference filters to select the wavelength. The absorption cross section of  $\text{O}_3$  at 254 nm was taken as  $5.0 \times 10^{-18} \text{ cm}^2$  [16].

### 2.1. Reagents

Chlorine dioxide was prepared by heating a moistened mixture of potassium chlorate and oxalic acid to 340 K in a stream of argon and trapping the OCIO at 195 K. Yields were about 35% based on  $\text{KClO}_3$ . Typically, 40 Torr of OCIO were stored in three 5 l blackened bulbs and usually diluted with 120 Torr of argon. Bromine was distilled from the reagent grade material. Nitric oxide was distilled from a Matheson cylinder, and ozonized oxygen was prepared by passing oxygen through a U-tube with nickel electrodes at 7.5 kV.

Flows of NO and of OCIO + Ar mixtures were controlled with stainless steel needle valves and were measured with calibrated glass ball flow meters.  $\text{Br}_2$  and  $\text{O}_3 + \text{O}_2$  flows entered the reactant cell through calibrated glass capillaries. Pressures were measured with a capacitance manometer (MKS Baratron model 222), and with a silicone oil manometer. To obtain maximum BrCl emission intensities, which were needed for the spectroscopic studies, the total flow was constricted in order to achieve a total pressure in the reaction chamber near 0.4 Torr. For actinometric measurements, the flow to the pump was unconstricted and the total reaction pressure was about 0.03 Torr for the  $\text{Br}_2 + \text{OCIO}$  experiments and about 0.1 Torr for the NO +  $\text{O}_3$  runs. Under these conditions, residence time in the cell was about 0.15 s.

## 3. Results and discussion

### 3.1. Spectrum of BrCl B–X from the $\text{Br}_2 + \text{OCIO}$ reaction

A low resolution survey spectrum of BrCl (B–X) is shown in Fig. 1(a). The assignments, based on Coxon's Franck–Condon factors [10], are the same as those of Clyne and Smith [8]; bands were observed with vibrational quantum numbers in the ranges  $0 \leq v' \leq 4$  to  $5 \leq v'' \leq 13$ . As in previous

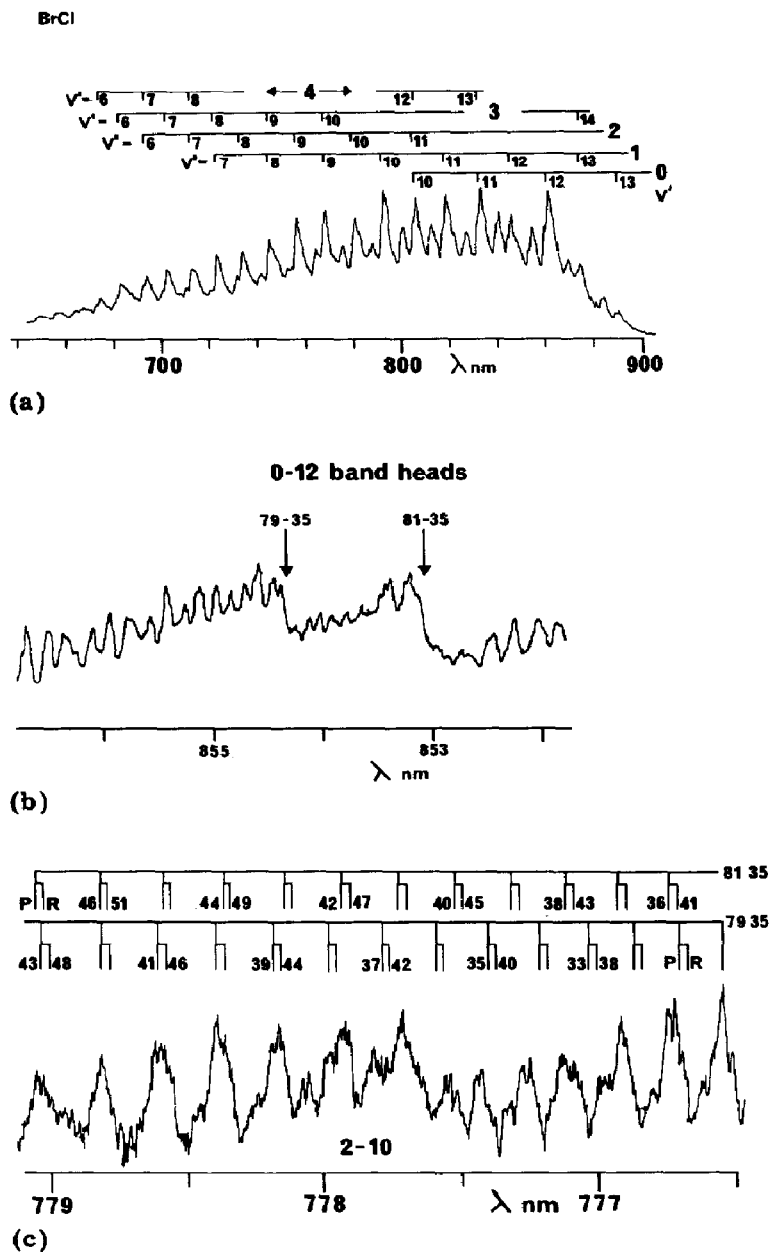


Fig. 1. Spectrum of the BrCl B-X chemiluminescence from the reaction  $\text{Br}_2 + \text{OClO}$ : (a) low resolution scan of the entire spectrum from 650 to 900 nm (assignments are  $v'-v''$  numbering of  $\text{Br}^{35}\text{Cl}$  bands); (b) medium resolution scan of part of the 0-12 band; (c) higher resolution scan of part of the 2-10 band, showing partial rotational resolution.

work [8], spectral analysis was performed only for the major isotopic species of  $^{79}\text{Br}^{35}\text{Cl}$  and  $^{81}\text{Br}^{35}\text{Cl}$ , although the weaker bands of  $^{79}\text{Br}^{37}\text{Cl}$  and  $^{81}\text{Br}^{37}\text{Cl}$  were clearly observed between the main bands. Figure 1(b) shows part of the 0-12 band at medium resolution (100 pm), from which

the major isotopic band heads are clear. In previous work [6 - 8], the 79-81 splittings of bromine in BrCl were not clearly resolved. Figure 1(c) shows partial rotational resolution at the highest practicable resolution (50 pm) for part of the 2-10 bands.

Rotational analyses were performed on the 0-12, 1-12, 0-11 and 2-10 bands as follows. Lines were assigned in the P and R branches of  $^{79}\text{Br}^{35}\text{Cl}$  and  $^{81}\text{Br}^{35}\text{Cl}$  for about 80  $J$  values. Most spectral features consisted of blends of P and R rotational lines of  $^{79}\text{Br}^{35}\text{Cl}$  and  $^{81}\text{Br}^{35}\text{Cl}$ ; the P-R doublet splitting is relatively small for both major isotopic species in these bands. Signal intensities were approximately  $10 \text{ photon s}^{-1}$  and it was impracticable to use higher resolution. The assignments were verified through forming combination differences  $\Delta F_2''(J)$  and  $\Delta F_2'(J)$  for both ground and excited states. The corresponding constants  $B_{v'}$  and  $B_v$  were determined using  $B_v = \Delta F_2(J)/4(J + \frac{1}{2})$  where centrifugal stretching has been neglected for the moderately low  $J$  states observed ( $J'' \leq 54$ ). Any anomalous pairs of data (*i.e.* P and R lines) were checked and re-assigned if necessary.

### 3.2. Determination of spectroscopic constants

The method of combination differences for the determination of rotational constants [17] leads to strongly overdetermined values, which are particularly seriously biased by errors in the data when extensive blending occurs, as in the present work. Therefore, the term value method described by Albritton *et al.* [18], which minimizes bias, was used to determine  $B_{v'}$  and  $B_v$ . Coxon's computer program [10], which is a variant of that described by Albritton *et al.* [18], was used for this purpose. The input data were the line wavelengths and  $J$  values, and three alternative sets of conditions were used to run the term value program: (a) with no constraints on the centrifugal stretching constants  $D_{v'}$ ,  $D_v$ ,  $H_{v'}$  and  $H_v$ ; (b) with these constants set equal to zero; (c) with these constants set equal to Coxon's values [10]. The range of  $J$  values in the present work did not extend to high enough values to define the centrifugal stretching terms; also, accuracy was limited owing to blending. As expected, therefore, the computed  $D_v$  and  $H_v$  values in case (a) were not reasonable and had large errors. Computed  $B_{v'}$  and  $B_v$  values were not strongly dependent on which set of assumptions (a), (b) or (c) was used for the  $D_v$  and  $H_v$  values. However, case (c) (using Coxon's values for the higher order rotational constants) was preferred since the bias in computed  $B_{v'}$  and  $B_v$  values should be minimized in this case.

Table 1 shows the computed values of  $B_{v'}$  and  $B_v$  and the band origins from term value analysis (case (c)) of the 0-12, 1-12, 0-11 and 2-10 bands of BrCl. Constants for the vibrational states  $7 \geq v'' \geq 1$  and  $8 \geq v' \geq 2$  have been determined from high resolution absorption spectroscopy [10]. Thus our values for  $B_2'$  ( $0.10462 \pm 0.00047 \text{ cm}^{-1}$  for  $^{79}\text{Br}^{35}\text{Cl}$  and  $0.10324 \pm 0.00055 \text{ cm}^{-1}$  for  $^{81}\text{Br}^{35}\text{Cl}$ ) may be compared directly with Coxon's determinations of  $B_2'$  which were  $0.10416 \pm 0.00002 \text{ cm}^{-1}$  and  $0.10339 \pm 0.00002 \text{ cm}^{-1}$  for  $^{79}\text{Br}^{35}\text{Cl}$  and  $^{81}\text{Br}^{35}\text{Cl}$  respectively. The agreement is good; it is clear that, notwithstanding the blending of rotational lines in our spectra, full

TABLE 1

Values of rotational constants  $B'_v$  and  $B''_v$  for  $^{79}\text{Br}^{35}\text{Cl}$  and  $^{81}\text{Br}^{35}\text{Cl}$ 

Transition	Origin $\bar{\nu}_{\text{vac}}$ ( $\text{cm}^{-1}$ )	$B'_v$ ( $\text{cm}^{-1}$ )	$B''_v$ ( $\text{cm}^{-1}$ )	No. of lines Standard deviation ( $\text{cm}^{-1}$ )	Reference
0-12 $^{79}\text{Br}^{35}\text{Cl}$	11699.98	0.10749	0.14322	88	this work
	$\pm 0.04$	$\pm 0.00039$	$\pm 0.00040$	0.23	
	11699.89	0.10705	0.14245		Coxon [6]
		$\pm 0.00005$	$\pm 0.00006$		
0-12 $^{81}\text{Br}^{35}\text{Cl}$	11718.22	0.10629	0.14179	94	this work
	$\pm 0.03$	$\pm 0.00022$	$\pm 0.00023$	0.15	
	11718.15	0.10627	0.14159		Coxon [6]
		$\pm 0.00005$	$\pm 0.00006$		
1-12 $^{79}\text{Br}^{35}\text{Cl}$	11912.33	0.10546	0.14236	83	this work
	$\pm 0.03$	$\pm 0.00045$	$\pm 0.00046$	0.27	
	11912.53	0.10575	0.14245		Coxon [6]
		$\pm 0.00005$	$\pm 0.00006$		
1-12 $^{81}\text{Br}^{35}\text{Cl}$	11929.97	0.10459	0.14130	91	this work
	$\pm 0.04$	$\pm 0.00032$	$\pm 0.00033$	0.22	
	11929.97	0.10498	0.14147		Coxon [6]
		$\pm 0.00005$	$\pm 0.00006$		
0-11 $^{79}\text{Br}^{35}\text{Cl}$	12097.26	0.10677	0.14301	73	this work
	$\pm 0.08$	$\pm 0.00040$	$\pm 0.00042$	0.22	
	12098.21	0.10705	0.14328		Coxon [6]
		$\pm 0.00005$	$\pm 0.00006$		
0-11 $^{81}\text{Br}^{35}\text{Cl}$	12114.77	0.10660	0.14331	85	this work
	$\pm 0.06$	$\pm 0.00033$	$\pm 0.00033$	0.21	
	12115.14	0.10627	0.14228		Coxon [6]
2-10 $^{79}\text{Br}^{35}\text{Cl}$	12917.61	0.10462	0.14488	70	this work
	$\pm 0.06$	$\pm 0.00047$	$\pm 0.00048$	0.26	
	12918.46	0.10444	0.14411		Coxon [6]
		0.10416 <sup>a</sup>			
2-10 $^{81}\text{Br}^{35}\text{Cl}$	12931.78	0.10324	0.14322	60	this work
	$\pm 0.11$	$\pm 0.00055$	$\pm 0.00058$	0.33	
	12932.45	0.10369	0.14349		Coxon [6]
		0.10339 <sup>a</sup>			

<sup>a</sup> Refers to directly measured  $B_v$  values; other data of ref. 6 cited in the table are by extrapolation.

advantage of the number of line measurements has been made to reduce error using the term value method of data reduction.

The present values for  $B'_0$ ,  $B'_1$ ,  $B''_{10}$ ,  $B''_{11}$  and  $B''_{12}$  are the first direct determinations to be reported. Table 1 includes a comparison of these data with the values obtained by extrapolation of Coxon's  $B_v''$  and  $B_v'$  functions

that were fitted to the ranges of  $v'$  and  $v''$  cited above. The agreement is generally satisfactory. The mean value of the isotopic ratio  $B_v(79)/B_v(81)$  from our work was 1.0077, which may be compared with the calculated value (*i.e.*  $\mu(^{79}\text{Br}^{35}\text{Cl})/\mu(^{81}\text{Br}^{35}\text{Cl})$ ) of 1.0076.

The measured band origin wavenumbers also confirm the extrapolated values from Coxon's work [10]; however, absolute wavenumbers cannot be expected to be more accurate than  $\pm 0.3 \text{ cm}^{-1}$  in view of the calibration errors of the spectrometer. Vibrational and rotational constants are now known or can be reliably interpolated for all stable levels of the  $B^3\Pi(0^+)$  excited state of BrCl and up to the level  $v' = 12$  of the  $X^1\Sigma^+$  ground state of BrCl.

### 3.3. Steady state vibrational energy distribution in the B state of BrCl

Relative vibrational populations were determined by measuring the relative intensities of specific rotational lines near the  $^{79}\text{Br}^{35}\text{Cl}$  band heads using the 4-6, 3-6, 3-7, 2-10, 1-10, 1-11, 0-11, 1-12 and 0-12 bands. These bands were chosen on the basis of calculations of Franck-Condon factors which showed less than a 20% overlap with other  $\text{Br}^{35}\text{Cl}$  bands. (Limited overlap was inevitable because of the presence of  $\text{Br}^{37}\text{Cl}$  bands and the tailing of rotational structure at the rotational temperature of 300 K.) The intensity data were treated using an approximate method, which was described by Clyne *et al.* [19] for the radiative combination of bromine atoms, as follows.

The bands appeared to show thermal rotational distributions at 300 K. Therefore, the intensities of lines near the band heads were assumed to be proportional to the integrated band intensities  $Q$ . Assuming the electronic transition moment does not vary with internuclear distance, the population  $N(v')$  of vibrational level  $v'$  is related to the integrated band intensity of the electronic emission band  $v'-v''$  by the expression

$$N(v') \propto Q/q_{v',v''} \nu^3$$

where  $q_{v',v''}$  is the Franck-Condon factor of the band and  $\nu$  is the frequency of the band origin. The results (Fig. 2) are shown in the form of a plot of  $\log(Q/q_{v',v''} \nu^3)$  versus  $\Delta U^\circ$ , the vibrational energy of the  $B^3\Pi(0^+)$  excited state above the potential energy minimum.  $\Delta U^\circ$  values have been given elsewhere [10].

Figure 2 shows that data for a common  $v'$  level and different  $v''$  levels gave essentially identical results, thus supporting the analysis we have used. The results showed that the steady state vibrational distributions at 2.7 Torr and 0.22 Torr were virtually identical.

The straight line corresponding to a Boltzmann distribution of vibrational energy in the B state of BrCl at 300 K is also included in Fig. 2. The experimental data for  $v' = 3$  and 4 suggest that a thermal Boltzmann distribution is approached in the upper part of the vibrational manifold. However, the data for the lower levels (see Fig. 2) indicate a flattening of the distribution between  $v' = 0$  and  $v' = 2$ . Thus the suggestion of Hadley *et al.* [7] that



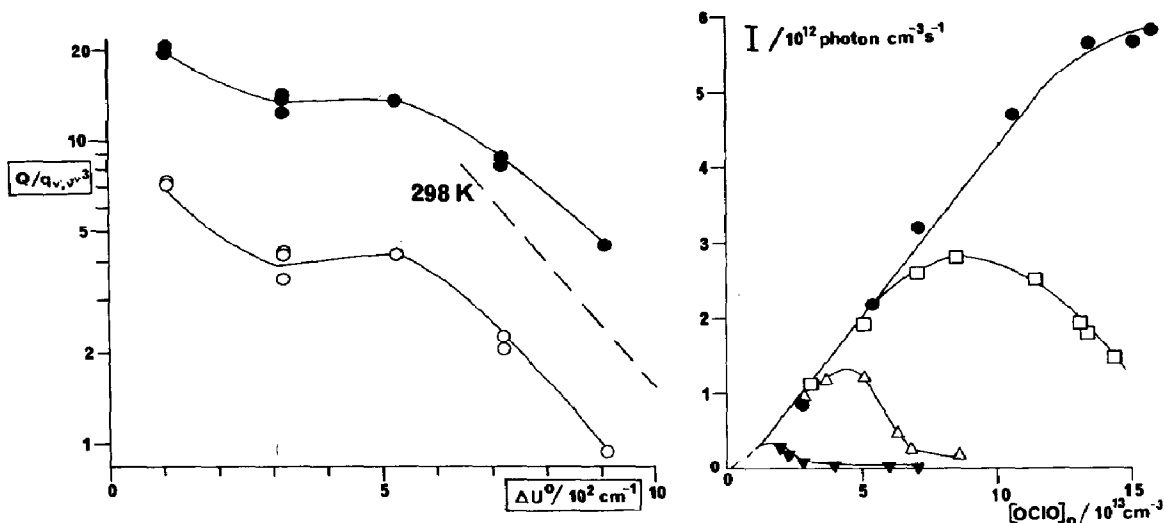
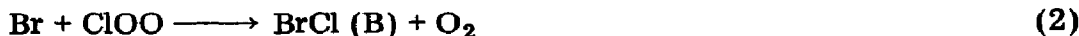


Fig. 2. Vibrational populational distribution in BrCl (B). The points are experimental data. The broken line corresponds to a Boltzmann distribution at 298 K.  $\Delta U^\circ$  is the energy of the  $v'$  state with respect to the potential energy minimum. ●, 0.22 Torr total pressure; ○, 2.7 Torr total pressure.

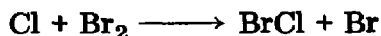
Fig. 3. Variation of BrCl chemiluminescence intensity with initial concentration of OClO and Br<sub>2</sub>. The run time was 70 ms. The measured intensity is the mean value over this time interval. Initial bromine concentration [Br<sub>2</sub>]<sub>0</sub> (10<sup>13</sup> cm<sup>-3</sup>): ●, 2.7; □, 1.1; △, 0.49; ▼, 0.22.

the steady state vibrational distribution within the B state of BrCl should be completely thermalized at pressures near 4 Torr is only partially supported by our results.

The presence of a maximum at  $v' = 2$  in the steady state distribution suggests that the reactive entrance channel which forms excited BrCl may cross the potential energy curve of the B state near the energy of the level  $v' = 2$ . The most probable reaction for forming excited BrCl B state molecules is the step



The stationary concentrations of Cl atoms in the Br<sub>2</sub> + OClO reaction are very small on account of the rapidity of the elementary step



$k^{298} = (1.9 \pm 0.2) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  [20]. Thus the third order chemiluminescent reaction  $\text{Br} + \text{Cl} + \text{M} \rightarrow \text{BrCl (B)} + \text{M}$  is excluded as the source of excited BrCl. The exoergicity of the Br + ClOO reaction can be calculated to be 185.0 kJ mol<sup>-1</sup> or 15470 cm<sup>-1</sup>, based on the most recent value [21]  $D_0^\circ(\text{BrCl}) = 17960 \text{ cm}^{-1}$  and the estimated value  $D_0^\circ(\text{ClOO}) = 29.3 \pm 6.0 \text{ kJ mol}^{-1}$  (2490 ± 500 cm<sup>-1</sup>) cited by Clyne and Watson [11].

The Br + ClOO reaction energy of  $15470 \pm 500 \text{ cm}^{-1}$  can be compared with the excitation energy of  $17155 \text{ cm}^{-1}$  for formation of the  $v' = 2$  state of

BrCl (B), as suggested above. Appreciable internal energy in the Br + ClOO reactants can be contributed, in addition, to the reactive collision. The energy match is considered reasonably satisfactory, in the light of the large uncertainty in the dissociation energy of the ClOO radical.

### 3.4. Photon yield of the Br<sub>2</sub> + OClO reaction

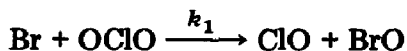
The total BrCl chemiluminescence emission intensity was measured as a function of reactant concentrations. Figure 3 shows the effect of varying initial OClO concentration, with the initial Br<sub>2</sub> concentration held constant at the values shown. For each value of [Br<sub>2</sub>]<sub>0</sub>, there was an initially linear dependence of chemiluminescence intensity *I* upon [OClO]<sub>0</sub>. At higher concentrations, a maximum value of *I* was observed and this behaviour is assigned to appreciable depletion of OClO and Br<sub>2</sub> concentrations along the reaction cell.

Absolute photon intensities from BrCl (B) were determined by reference to the light output from the chemiluminescent NO + O<sub>3</sub> reaction under the same experimental conditions. The NO + O<sub>3</sub> reaction forms excited NO<sub>2</sub>\* which emits in the red and IR spectral regions [14, 15]. Using previous work [14], the NO<sub>2</sub>\* emission intensity (in photon cm<sup>-3</sup> s<sup>-1</sup>) was assumed to be given by the relation  $I_{\text{NO}_2^*} = 1.55 \times 10^{-2} [\text{NO}][\text{O}_3]/[\text{O}_2]$  for  $\lambda \leq 875$  nm. For typical conditions with [Br<sub>2</sub>]<sub>0</sub> = [OClO]<sub>0</sub> = 2.3 × 10<sup>13</sup> cm<sup>-3</sup>, the observed BrCl\* photon flux *I* was determined to be 7.1 × 10<sup>11</sup> photon cm<sup>-3</sup> s<sup>-1</sup>. The corresponding stationary concentration of excited BrCl\* molecules is given by the expression

$$[\text{BrCl}^*] = 7.1 \times 10^{11}/k_{\text{R}}$$

where  $k_{\text{R}} = 1/\tau_{\text{R}}$  is the rate constant for spontaneous emission from BrCl (B). According to Clyne and McDermid's [21] recent laser-induced fluorescence work on BrCl,  $\tau_{\text{R}} = 40 \mu\text{s}$ , which gives  $[\text{BrCl}^*] = 2.8 \times 10^7 \text{ cm}^{-3}$ .

The photon yield for the Br<sub>2</sub> + OClO reaction may be estimated in several ways. The most conservative approach is to assume that the reaction



was rate controlling and that  $[\text{Br}] \ll [\text{Br}_2]$ . The overall photon yield defined on this basis was

$$\Phi \geq I/k_1 [\text{Br}_2] [\text{OClO}] \quad (\text{I})$$

and a lower limit value for  $\Phi$  was determined to be  $3 \times 10^{-3}$  using the typical initial concentrations  $[\text{Br}_2]_0 = [\text{OClO}]_0 = 2.3 \times 10^{13} \text{ cm}^{-3}$  and  $k_1 = 4.2 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 300 K from ref. 11. Equation (I) is consistent with the observed linear dependence of *I* on [OClO]<sub>0</sub> at low OClO concentrations

### 3.5. Reaction mechanism

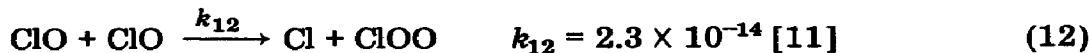
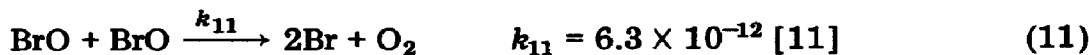
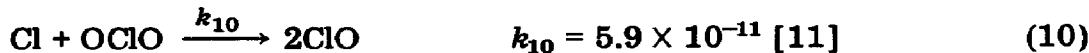
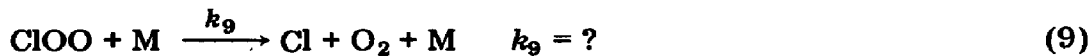
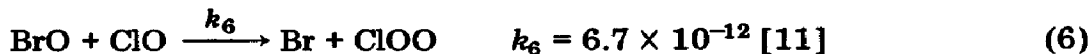
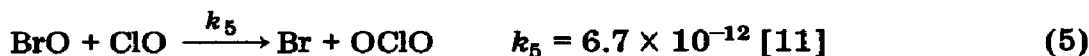
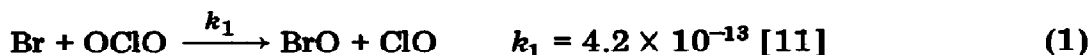
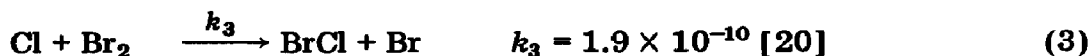
The value of  $\Phi$  for the overall quantum yield is clearly a lower limit and is known to depend on the concentrations of reagents. Based on Clyne and

Watson's study of reactions involving ground state species in the Br + OClO reaction [11], a reaction mechanism for emission of BrCl chemiluminescence in the Br<sub>2</sub> + OClO reaction may be proposed. The significance of the value  $\Phi \geq 3 \times 10^{-3}$  is discussed in the light of this mechanism.

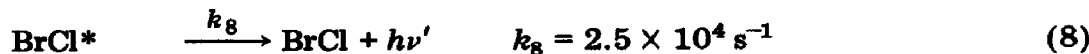
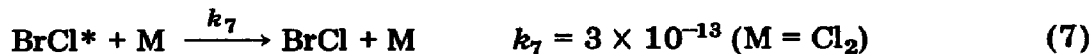
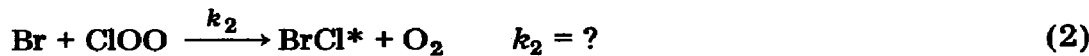
The Br<sub>2</sub> + OClO reaction is considered to be a simple branched-chain reaction, in which the initiation step is uncertain but may be



The subsequent ground state reactions and their rate constants at 298 K ( $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ) have been characterized by Clyne and Watson [11] and by Bemand and Clyne [20]:



In this scheme, reaction (1) is the chain-branching step. Excited BrCl\* is assumed to be formed by reaction (2); BrCl\* (B) molecules may be deactivated either by electronic quenching (7) or by radiation (8). The rate constants for both these processes (7) and (8) have been determined by Clyne and McDermid [12] and by Wright *et al.* [13]:



Quenching of BrCl\* (reaction (7)) was negligibly slow under our experimental conditions.

Computer simulations of the Br<sub>2</sub> + OClO reaction were carried out by numerical integration of the coupled rate equations in the above scheme [11], together with an additional step, namely first order wall recombina-

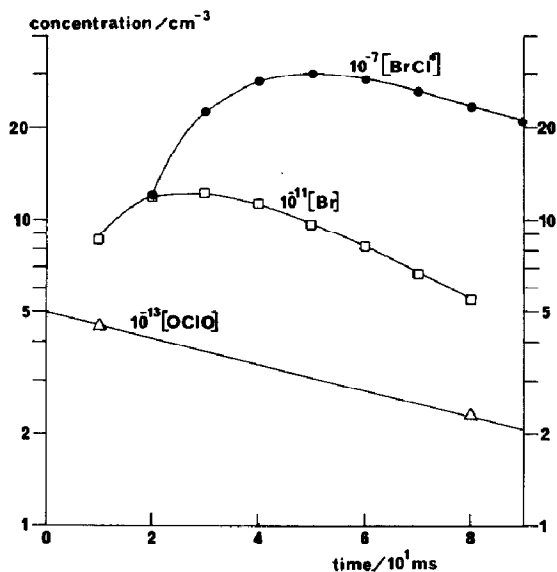


Fig. 4. Computed variations of concentration with time. The chemiluminescence intensity  $I$  follows the  $[\text{BrCl}^*]$  curve. Note that the branching ratio for forming  $\text{BrCl}^*$  in reaction (2) has been assumed to be 0.1.

tion of Br atoms with a rate constant of  $50 \text{ s}^{-1}$  [11]. Wall loss of ClO and BrO radicals is insignificant compared with homogeneous reaction of these species [11]. The rate constants cited were used as fixed parameters, and the rate constants  $k_2$ ,  $k_4$  and  $k_9$  were varied.

As expected, above a threshold value  $k_4 \geq 3 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  the initiation rate had little effect on the formation of maximum concentrations of radicals. Lower values of  $k_4$  were considered unreasonable since a slow build-up of radicals and of  $[\text{BrCl}^*]$  then occurred, lasting over 1 s; whereas the BrCl chemiluminescence intensity always rapidly built up close to the  $\text{Br}_2 + \text{OClO}$  mixing region, on a time scale of 10 - 100 ms. With  $k_4$  fixed at  $1 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , the values of  $k_2$  and  $k_9$  were varied in order to simulate the observed range of  $\text{BrCl}^*$  concentration ( $10^7 - 10^8 \text{ cm}^{-3}$ ) and the time for  $\text{BrCl}^*$  to reach its maximum value. A range of magnitudes of  $k_2$  and  $k_9$  was consistent with the results and typical values were  $k_2 = 1.0 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  and  $k_9 = 1 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ .

Figure 4 shows the computed variations with time of  $[\text{Br}]$  and  $[\text{BrCl}^*]$  using  $k_2 = 1.0 \times 10^{-10}$  and  $k_4 = k_9 = 1 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , and with  $[\text{Br}_2]_0 = 1.1 \times 10^{13} \text{ cm}^{-3}$ ,  $[\text{OClO}]_0 = 5.0 \times 10^{13} \text{ cm}^{-3}$ , simulating data of Fig. 3. The values of  $[\text{BrCl}^*]$  do not vary greatly during the 70 ms of reaction time, which agrees with the observation of a nearly uniform chemiluminescence intensity distribution along the reaction cell. The ratio  $[\text{Br}]/[\text{Br}_2]$  has a mean value of about 0.1 according to the computed concentration profiles. We note that the magnitude of  $[\text{Br}]/[\text{Br}_2]$  was insensitive to the magnitude of  $k_4$  and  $k_9$ , as would be expected.

Therefore, an improved lower limit for the overall quantum yield may be obtained:

$$\Phi_{\text{Br}} = I/k_1[\text{Br}][\text{OCIO}] \approx 3 \times 10^{-2}$$

where  $[\text{Br}]$  has been taken to be equal to  $0.1[\text{Br}_2]$ . This value of  $\Phi_{\text{Br}}$ , when applied to the typical concentration conditions,  $[\text{Br}_2]_0 = [\text{OCIO}]_0 = 2.3 \times 10^{13} \text{ cm}^{-3}$ , indicates that one photon was emitted for reaction between 30 bromine atoms and 30 chlorine dioxide molecules. The computer profiles predict somewhat higher  $[\text{BrCl}^*]$  values than the experimental results which indicate that the branching ratio for forming  $\text{BrCl}^*$  in reaction (2) is less than unity.

Comparison of the experimental variations of chemiluminescence intensity  $I$  with  $[\text{OCIO}]_0$  and  $[\text{Br}_2]_0$ , with computed results, over the run time of 70 ms, was made. The agreement is satisfactory, if a branching ratio of 0.1 is chosen for formation of  $\text{BrCl}^*$  in reaction (2). However, other combinations of the unknown rate constants  $k_2$  and  $k_9$  can also be expected to fit the data, although a branching ratio less than 1 is implied for reaction (2) by all the models.

The present work and the earlier study of Clyne and Watson [11] thus provide at least a qualitative explanation of the spontaneous reaction of  $\text{Br}_2$  with  $\text{OCIO}$ , and the self-decomposition of  $\text{OCIO}$  [6]. Both processes are characterized as branched-chain reactions which require the initiation rate to compete successfully against the termination rate for reaction to occur. In the  $\text{Br}_2 + \text{OCIO}$  reaction, the slow chain-branching step  $\text{Br} + \text{OCIO} \rightarrow \text{BrO} + \text{ClO}$  is rate controlling and the chain is rapidly propagated by the  $\text{BrO} + \text{ClO}$  and  $\text{BrO} + \text{BrO}$  reactions. Branching in the self-decomposition of  $\text{OCIO}$  occurs by the rapid step  $\text{Cl} + \text{OCIO} \rightarrow 2\text{ClO}$ , but in this case regeneration of the  $\text{Cl}$  atom chain carrier is blocked by the slow rate of the bimolecular  $\text{ClO} + \text{ClO}$  reactions. Thus, the  $\text{Br}_2 + \text{OCIO}$  reaction is initiated much more easily and the self-decomposition of  $\text{OCIO}$  occurs only at pressures in the torr range [6].

## Conclusions

It is concluded that the  $\text{Br}_2 + \text{OCIO}$  overall reaction has a fairly high photon yield; using partial pressures of  $\text{Br}_2$  and  $\text{OCIO}$  equal to 1 mTorr, one photon is emitted for reaction between thirty  $\text{Br}$  atoms and  $\text{OCIO}$  molecules. (The photon yield is 50% greater [8] if account is taken of chemiluminescence at wavelengths above 875 nm, which could not be detected in the present work.) Stationary  $\text{BrCl}(\text{B})$  excited state concentrations in excess of  $10^8 \text{ cm}^{-3}$  were observed under these conditions. The low efficiency of electronic quenching of  $\text{BrCl}(\text{B})$  [9, 13] is favourable for scaling the  $\text{Br}_2 + \text{OCIO}$  chemiluminescent reaction to higher pressures.

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