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A Novel Chemiluminescent Reaction: the Detection of an Electronic Emission Spectrum of BrCl

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There is definite evidence for only two or three exothermic transfer reactions of simple molecules in which the energy of reaction appears largely as electronic excitation in the product molecules; these include the reactions of (i) NO with O_3,[1] and (ii) N with CH and CCl.[2] In the present work, we have detected chemiluminescent emission from electronically-excited BrCl molecules formed directly in the transfer reaction between bromine atoms and chlorine dioxide:—

$$Br + ClO_2 \rightarrow BrCl + O_2 + 49\,\text{kcal.mole}^{-1} \quad (1)$$

When bromine atoms (from a high-frequency electric discharge in Br_2 + Ar mixtures) are mixed with chlorine dioxide in a fast flow system at total pressures between 1 and 4 mm. Hg, rapid reaction occurs, and a deep red glow is emitted from the reaction zone. A rapid reaction between chlorine dioxide and *molecular* bromine could be initiated in this pressure range using lower flow velocities by slight warming or sparking of the mixed gases. The same red glow was visible in this system, as was observed in the reaction of atomic bromine with chlorine dioxide.

The spectrum of this chemiluminescent emission, when photographed in the 1st and 2nd orders of a high-speed grating spectrograph, was found to extend from 5700 Å up to 8800 Å (the low energy cut-off of the film emulsion), and to consist of a large number of red-degraded bands. The wavenumbers of the heads of 43 bands of a strong system have been measured to within ± 3 cm.$^{-1}$, and the positions of the heads of several other weaker bands of the same system have been located to within ± 10 cm.$^{-1}$ At the lower-energy end of the spectrum, two progressions ($v' = 0$ and $v' = 1$) in the ground, state vibrational quantum number, v'', are prominent, and in this region a second, less intense, pair of progressions of bands lying to the higher-energy side of the main bands are also observed. The strong progressions are identified as a transition from the low-lying $^3\Pi_1$ excited state to the $^1\Sigma^+$ ground state of $Br^{35}Cl$; while the weaker, related progressions are due to the same transition of the less-abundant, isotopically heavier $Br^{37}Cl$ molecule. (The bromine 79/81 isotopic splitting was not resolved with the low-dispersion spectrograph used, except for one or two of the lowest-energy bands). From the magnitudes of the chlorine isotopic splittings, the vibrational numbering of both states was found, and from the complete vibrational analysis, the following constants (in cm.$^{-1}$) for the two states of $Br^{35}Cl$ are reported:—

$$\nu_e = 16{,}815 \pm 2;\ \omega_e'' = 435 \pm 1;$$
$$\omega_e''x_e'' = 1{\cdot}5 \pm 0{\cdot}1$$
$$\nu_{00} = 16{,}705 \pm 2;\ \omega_e' = 217 \pm 2;$$
$$\omega_e'x_e' = 6{\cdot}7 \pm 0{\cdot}3$$

Herzberg[3] has given a value of 430 cm.$^{-1}$ for ω_e'' based on a vibrational analysis of two u.v.

absorption systems[4] of BrCl. However, the vibrational interval $\Delta G''(\frac{1}{2})$ was found to vary between 407 and 440 cm.$^{-1}$ [4] and it is clear that our value for ω_e'' has much greater reliability. It is interesting that BrCl is the only one of the six possible diatomic interhalogens whose visible spectrum, $(^3\Pi \longleftrightarrow {}^1\Sigma^+)$, has hitherto escaped observation either in absorption or emission, and whose vibrational constants have been uncertain.

The emission spectrum obtained from a mixture of chlorine atoms and bromine atoms was also recorded, and in the region $\lambda > 7000$ Å, all the bands were identical to those of BrCl described above. At higher energies, there was considerable overlapping of the BrCl bands by the chlorine afterglow bands,[5–7] $[Cl_2(^3\Pi_{ou^+} \rightarrow {}^1\Sigma_g^+)]$; no Br_2 bands could be detected.

A similar band system $[ICl(^3\Pi_1 \rightarrow {}^1\Sigma^+)]$ has also been identified in emission from mixtures of chlorine atoms and iodine atoms.[7]

It is significant that no chlorine afterglow bands (or bromine bands) were present in the $Br_2 + ClO_2$ reaction zone. It follows that in the $Br_2 + ClO_2$ reaction, the excited state of BrCl is populated directly by the transfer reaction (1), and not by radiative combination of a bromine atom and a chlorine atom, as is observed in the Br + Cl experiments:—

$$Br + Cl(+M) \rightarrow BrCl(+M) + 54 \text{ kcal.mole}^{-1} \quad (2)$$

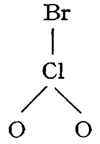
This conclusion is confirmed by the observation of greatly different populations of the vibrational levels of the upper state of BrCl in the $Br_2 + ClO_2$ and Br + Cl experiments; in the $Br_2 + ClO_2$ system, the populations of the lower levels ($v' = 0,1,2$) are relatively greater than in the Br + Cl atom recombination reaction.

Finally, the nature of the $Br_2 + ClO_2$ reaction suggests that a chain reaction involving atomic bromine as chain carrier occurs:

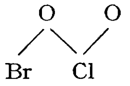
$$Br + ClO_2 \rightarrow BrCl^* + O_2,$$

$$Br_2 + BrCl^* \rightarrow 2Br + BrCl.$$

The formation of $BrCl^*(^3\Pi_1)$ suggests that the reaction occurs *via* a triangular transition state (I), rather than *via* a chain (II).



(I)



(II)

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