The Kinetics of the Nitrogen Afterglow

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THE yellow afterglow of active nitrogen is due mainly to emission of the First Positive bands of $N_2(B^3\Pi_g \rightarrow A^3\Sigma_u^+)$ from levels below the dissociation limit.[1] Although it is generally agreed that the intensity of the afterglow is proportional to the square of the concentration of ground state nitrogen atoms, its pressure dependence is less clearly established. Lord Rayleigh's experiments[2] indicate that the intensity is proportional to the nitrogen pressure up to about 0·2 mm. Hg. Later workers[3,4] have assumed this relationship to be correct between 0·1 and 1·0 mm. Hg and even up to atmospheric pressure,[5] although their experimental data did not clearly establish it. Later work[6] showed the quantity $I/[N]^2$ to be almost independent of pressure in the range 1—10 mm. Hg. Partial replacement of nitrogen by argon enhances the afterglow[1] and this has been attributed to an increased rate of recombination with argon as third body.[7] Recently Young, Sharpless, and Stringham[8] have observed considerable enhancement of the afterglow using 1% of nitrogen in a helium carrier, its intensity being proportional to pressure up to a few mm. Hg. They suggest that molecular nitrogen quenches some intermediate efficiently, the half-quenching pressure being of the order of 0·04 mm. Hg.

We have investigated these processes in a discharge–flow system at room temperature and find that the rate constants, expressed as $d[N_2]/dt$, for the recombination of nitrogen atoms at 20°c with argon or helium as third bodies (1·73 and $1{\cdot}92 \times 10^{15}$ cm.^{6} mole^{-2} sec.$^{-1}$, respectively) are only about 25% greater than with nitrogen as third body ($1{\cdot}38 \times 10^{15}$ cm.^{6} mole^{-2} sec.$^{-1}$). The intensity (I) of the afterglow is proportional to the square of the nitrogen atom concentration and independent of pressure between 2 and 10 mm. Hg for pure nitrogen. When nitrogen was partially replaced with argon, the ratio $[N]^2/I$ increased linearly with the mole fraction of molecular nitrogen present but was independent of total pressure. The dependence of this quantity on composition rather than on pressure shows that the dominant processes forming and removing N_2 in the $B^3\Pi_g$ state are collision controlled. The

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extrapolated intensity for pure argon is six times greater than for pure nitrogen. This together with the Stern–Volmer type dependence of the intensity on mole fraction of nitrogen indicates that molecular nitrogen in its ground state is an effective quenching agent for the $B^3\Pi_g$ state of nitrogen.

Jeunehomme and Duncan[9] have recently measured the lifetimes of the relevant vibrational levels of the $B^3\Pi_g$ state of nitrogen and their pressure dependence. Since the rate of light emission in a chemiluminescent reaction is the product of the rate of formation of the excited species and its fluorescence efficiency[10] the rate constant for nitrogen atom recombination *via* the $B^3\Pi_g$ state of N_2 can be calculated from their data and the absolute intensity of N_2 First Positive emission. For the latter we obtain 7×10^6 cm.^{3} mole^{-1} sec.$^{-1}$ expressed as a second order rate constant in pure nitrogen over the range 2—10 mm. Hg, using the air afterglow for calibration.[11] When combined with the quenching data,[9] this gives a rate constant of 5×10^{14} cm.^{6} mole^{-2} sec.$^{-1}$ for the recombination *via* the $B^3\Pi_g$ state with N_2 as a third body.

This relatively large value apparently excludes mechanisms for the nitrogen afterglow[3] which postulate appreciable steady-state populations of the very shallow $^5\Sigma_g^+$ state of N_2. Present data, particularly on the dependence of the vibrational distribution in the $B^3\Pi_g$ state on the third body used[1] support the view that the $A^3\Sigma_u^+$ state is the precursor of the afterglow, since the relevant vibrational levels of the B state have energies and turning points close to those of the A state. We cannot however exclude an alternative mechanism in which two nitrogen atoms approach each other along the $^5\Sigma_g^+$ potential surface and a collision transfers them to the $B^3\Pi_g$ with loss of energy, providing the overall process is kinetically third order.

The observed half-quenching pressure for the relevant levels of the $B^3\Pi_g$ state by nitrogen is 0·25 mm. Hg. Below this pressure the afterglow in pure nitrogen should tend to third order kinetics ($\propto[N]^2[N_2]$) and above this to second order ($\propto[N]^2$) with the rate constants given in the penultimate paragraph. Most of the published data support this view.[2–4,6,8] In particular, Noxon's data,[5] if re-interpreted taking the nitrogen afterglow intensity to be independent of nitrogen pressure up to one atmosphere, agree with our constants within a factor of two, without the need to assume either additional reactions removing nitrogen atoms or unduly high nitrogen atom concentrations.

For mixed carriers the intensity at high pressures will depend on the composition but not on the total pressure as observed here and in experiments with added ammonia.[1] The form of this dependence and the high intensities obtained with inert gases as carriers show that the rate of quenching of the $B^3\Pi_g$ state of N_2 depends much more on the species involved than does the rate of formation. It follows that the pressure at which the fall-off to third order emission kinetics occurs is much higher with less efficient quenchers such as the inert gases than with nitrogen. It will be lower still for systems containing gases such as ammonia which quench the $B^3\Pi_g$ state of N_2 at every collision.

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