The Role of N_2 ($A^3\Sigma_u^+$) Molecules in Active Nitrogen

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IT is well known that flowing active nitrogen contains at least one metastable species of high energy, which can readily excite many additives, especially metal and metal salt vapours.[1] Emission can be detected from levels which demand transfer of almost the full recombination energy of nitrogen molecules.[2,3] A review of *actual* lifetimes of excited species in the nitrogen afterglow[4] has shown that species of sufficient energy to give these effects could not persist from the discharge under normal conditions.

We report that metastable nitrogen molecules, formed by three-body recombination, dissociate gases which are immune to direct attack by nitrogen atoms.

The experimental system has been described previously,[5] as has the photometric observation of oxygen atom production resulting from the decomposition of carbon dioxide and nitrous oxide added well beyond the discharge.[6] An extensive study for additions of 10—50% of these to active nitrogen at 2—6 mm. Hg total pressure has shown that the rate of production of oxygen atoms is proportional to the square of the nitrogen atom concentration and to the total pressure, but is virtually independent of carrier composition, including experiments where some 60% of argon was added to the system to increase the steady-state concentration of $N_2(B^3\Pi_g)$, which emits the First Positive system.[5] Direct reaction with nitrogen atoms has been excluded previously.[6]

Addition of 10—30% of water vapour to active nitrogen at 298° K gave a similar production of oxygen atoms, showing substantially the same behaviour as carbon dioxide and nitrous oxide systems at 196° K. Thermochemical considerations rule out direct nitrogen atom reaction.

Kinetic analysis showed that some 50—70% of nitrogen atom recombination resulted in decomposition of the additive providing sufficient additive was present.

Dunford[7] examined the decomposition of ammonia by active nitrogen at 300° K, where direct reaction with nitrogen atoms does not occur.[8] Recently these results have been re-interpreted[3] to show that the decomposition is due to an excited molecular species formed by three-body recombination, a large fraction of recombinations giving rise to decomposition as observed for CO_2, N_2O, and H_2O in our study. This system was complicated by the facts that the products were not observed directly and there are secondary reactions involving nitrogen atoms.[9]

To explain these kinetics and the efficiency of the processes, $N_2(A^3\Sigma_u^+)$ must be considered to be responsible for the bulk of the decompositions. If stabilisation of the weakly bound $N_2(^5\Sigma_g^+)$ state is a minor process,[5] then statistically $N_2(A^3\Sigma_u^+)$ should be formed by 75% of recombinations. Our results suggest that most of it produces direct dissociation of the additive.

$$N_2(A^3\Sigma_u^+) + CO_2(^1\Sigma_g^+) = N_2(X^1\Sigma_g^+) + CO(^1\Sigma_g^+) + O(^3P) \quad (1)$$

$$N_2(A^3\Sigma_u^+) + N_2O(^1\Sigma) = N_2(X^1\Sigma_g^+) + N_2(X^1\Sigma_g^+) + O(^3P) \quad (2)$$

$$= N_2(X^1\Sigma_g^+) + NO(^2\Pi) + N(^4S) \quad (2a)$$

$$N_2(A^3\Sigma_u^+) + H_2O(^1A_1) = N_2(X^1\Sigma_g^+) + OH(^2\Pi) + H(^2S) \quad (3)$$

These reactions show overall spin conservation and are all exothermic, $N_2(A^3\Sigma_u^+)$ having a minimum energy of 143 kcal./mole. Processes (4) and (5)

$$N + OH = H + NO \quad (4)$$

$$N + NO = N_2 + O \quad (5)$$

have rate constants $> 10^{13}$ cm.^{3} mole^{-1} sec.$^{-1}$ (ref. 10 and 11), so that the only detectable product of reaction will be oxygen atoms. A concurrent reaction with the shorter lived $N_2(B^3\Pi_g)$ state is not excluded as a relatively minor process.

Brennen and Kistiakowsky[3] have shown that Ni, Fe, and Hg atoms are excited by a species which is a major product of nitrogen atom recombination. They suggest that this species is $N_2(A^3\Sigma_u^+)$, which is removed on the walls and can excite metal atoms at almost every collison providing spin is conserved. From the kinetic behaviour of CN violet emission in active nitrogen and its failure to extend to the vessel walls, we have shown that the species responsible for exciting CN is formed by nitrogen atom recombination and is removed on the walls.[12] This process occurs efficiently under conditions where $[CN] \approx 1/1000\ [N]$ (ref. 13). In both sets of work, the emission is efficiently quenched by ammonia[3,13] and it is now clear that this "quenching" process involves the spin-allowed dissociation of ammonia by $N_2(A^3\Sigma_u^+)$.

All of these observations support the previous conclusion[5] based on studies of the nitrogen afterglow that the $A^3\Sigma_u^+$ state of N_2 is populated by more than half of the nitrogen atom recombinations. This work showed that the $B^3\Pi_g$ state of N_2, which emits the yellow afterglow, is populated from high vibrational levels of $N_2(A^3\Sigma_u^+)$. The effect of additives on this emission[14] and on metal atom emission[3] shows that these higher levels of $N_2(A^3\Sigma_u^+)$ have shorter lives than lower levels; this must be due to vibrational relaxation.

The experiments cited here indicate that wall removal is the process which limits the concentration of the $N_2(A^3\Sigma_u^+)$ state in active nitrogen at low pressures, so that its Vegard–Kaplan band emission cannot be detected.[15] Noxon's experiments[16] at higher pressures show that $N_2(A^3\Sigma_u^+)$ is little quenched by ground state N_2; his data can be reinterpreted to show that removal by nitrogen atoms is its dominant decay at pressures approaching one atmosphere.[17] Although it can be shown that the steady-state concentration of $N_2(A^3\Sigma_u^+)$ is $< 10^{-3}[N]$ for active nitrogen in the mm. pressure range, its reactions cannot be neglected because of its high efficiency of energy transfer in spin-allowed processes; by comparison, the reactions of ground-state nitrogen atoms with many species are endothermic or spin-forbidden.

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