ACTIVE NITROGEN INDUCED CHEMILUMINESCENCE AT SODIUM SULFATE SURFACES

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The existence of a layer of free alkali metal atoms in the upper terrestrial atmosphere, near 95 km altitude, has been known for almost fifty years [1]. However, the mechanisms for the production and nighttime excitation of these atomic species, which are observed by their resonance fluorescence at high altitude, are still a matter for conjecture. It has been suggested that a dust layer may exist in the vicinity of the electronically excited transient metal atoms [2, 3], which could act as a source for their continual production. Thus, it is conceivable that heterogeneous processes, involving the interaction of ambient gaseous atmospheric constituents with dust-particles, could play a role in this natural phenomenon. Consequently, investigations of heterogeneous reactions between gaseous reactive intermediates, mainly atoms and free radicals, and various metal salts have been conducted in the authors laboratory [4-7] with a view to identifying those processes which might contribute to excited alkali metal atom production and excitation in the E-region of the ionosphere and in aurora. During the course of these investigations it was observed that anhydrous sodium sulfate visually emitted an intense blue-green glow when exposed to a flowing afterglow of 'active' nitrogen. Spectroscopic examination of this emission revealed the simultaneous presence of electronically excited sodium atoms (Na) and singly positive charged nitrogen molecules (N_2^+), specifically associated with the salt surface [5-7]. Here, we shall report on additional studies of this unique heterogeneous chemiluminescent reaction system.

The apparatus and reagents used in these experiments have been described in detail elsewhere [5, 6]. Briefly, 'active' nitrogen was generated in a low-pressure, fast-flow system by maintaining an electrodeless microwave discharge in type E, 'dry, high-purity' nitrogen. Microscope slides coated with sodium sulfate were suspended in the flow reactor and located approximately 50 msec downstream from the discharge source. In most cases, the salt surface was then preconditioned to the low-pressure, flowing afterglow prior to making quantitative observations of the chemiluminescence. The visible emission from the coated-slide surface was focussed on the entrance slit of a 0.5 meter Jarrell-Ash scanning spectrometer. A Keithley electrometer operating in the nanoamp to microamp ranges was used to amplify the output of the IP28 photomultiplier detector and the spectral intensity distribution was recorded as a function of wavelength in the range 578 to 591 nm, at a scanning speed of 1 nm/min. Absolute N atom concentrations were determined by titrating the afterglow to extinction with a measured flow of 'prepurified' nitric oxide. Great care was taken to ensure the integrity of the 'conditioned' salt

surfaces between experiments by maintaining continual flow of 'undischarged' nitrogen through the system. This precaution was necessary to obtain reproducible results.

The nature of the heterogeneous chemiluminescent reaction was studied at room temperature by simultaneously observing the variation in the intensities of emissions at 580.4 nm and at 589.0 and 589.6 nm as a function of experimental variables. The former emission results from the transition N_2 $(B^3\Pi, v' = 11 \rightarrow A^3\Sigma, v'' = 7)$ in the nitrogen first positive band system [8], whereas the latter emissions are the well known sodium D lines, which result from the electronic transitions NaD_2 $(3^2P_{3/2} \rightarrow 3^2S_{1/2})$ and NaD_1 $(3^2P_{1/2} \rightarrow 3^2S_{1/2})$, respectively. Heterogeneity of the chemiluminescence was established by the following observations: 1). The visible blue-green glow was obtained only from glass slides coated with anhydrous sodium sulfate and not from uncoated slides suspended in the flowing afterglow; 2). There was no evidence of emission corresponding to electronically excited Na or N_2^+ either upstream or downstream of the coated slide; 3). Upon exposing a freshly coated slide to 'active' nitrogen, maintained at a constant concentration in $N(^4S)$ atoms, the intensities of the sodium D lines were initially zero but increased linearly with exposure time over a period of several hours and finally levelled off at a saturation condition after about 6 hrs exposure. This effect indicated that atomic sodium was not present initially but was produced as a result of reaction, probably at the surface of the salt, with one or more energetic species in 'active' nitrogen. As a consequence, all freshly coated slides were subjected to at least 6 hrs exposure in 'active' nitrogen prior to quantitative spectroscopic observations; 4). The anhydrous sodium sulfate changed color from white to light blue following prolonged exposure to the flowing afterglow. This change in the physical character of the salt may be attributed to the accumulation of interstitial atomic sodium and/or free electrons in the crystal lattice.

The relationship between the emission intensity at 580.4 nm (N_2^*) and the $N(^4S)$ atom concentration in 'active' nitrogen was determined by the NO 'titration' method. It was found that,

$$[N]^{1.5\pm0.15} \, \alpha \, I_{N_2}*(\lambda = 580.4 \text{ nm})$$

under the conditions of temperature (297°K) and pressure (3-5 Torr) employed. At concentrations $> 2 \times 10^{14}$ N atom cm^{-3} the ratios of the sodium D line intensities (NaD_1/NaD_2) were constant at 1.96 $\pm$ 0.02, but they showed a dependence upon N_2^* emission according to the relation:

$$I_{NaD_1} \, \alpha \, I_{NaD_2} \, \alpha \, [I_{N_2}*]^{1.3}$$

This suggests that, $\quad I_{NaD_1} \, \alpha \, I_{NaD_2} \, \alpha \, [N]^2$

However, the energy required for the liberation of an electronically excited sodium atom from the crystal lattice ($\sim$ 12 ev) or the production of $N_2^+(B^2\Sigma, v' = 3)$, which requires 19.6 ev, greatly exceed that liberated by the simple recombination of two $N(^4S)$ atoms (9.8 ev). Thus, it appears that the derived relationship above oversimplifies the complex nature of the overall heterogeneous reaction. It is necessary, therefore, to invoke the

participation of a more energetic species in 'active' nitrogen in order to explain the observed chemiluminescence. The importance of various energetic species will be discussed in the context of recent theories, which have been developed to explain the nature of 'active' nitrogen [9].

Acknowledgement

References

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