THE REACTION BETWEEN NITRIC OXIDE AND ATOMIC OXYGEN

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The scarcity of chemiluminescent reactions has been noted by many observers. There appear to be almost no reactions known in which there is a stoichiometrical relation between the light emitted and the chemical reaction. Often there is only one quantum of light emitted for a very large number of reacting molecules, so that one may not be sure that he has observed the reaction which produces the light emission at all. It could not be expected, of course, that reactions in, or at the surface of, condensed phases would be particularly efficient, since collisions of the second kind might be expected to convert much of the energy of excitation into thermal energy before it could be radiated. The condition most favorable to chemiluminescence is, therefore, to be found in a gas at low pressures, and it is under these conditions that the "afterglow" reactions take place.

The similarity between the conditions necessary for an afterglow, and the conditions prevailing in the nebulae and in auroral discharges has been recognized for a long time by physicists.

The simplest chemiluminescent process is the formation of a molecule in an excited electronic state from molecules or atoms in a normal state. By the term "normal state" we mean to rule out excited or even metastable electronic states of molecules or atoms, since such do not have a sufficiently long life to participate in chemical reaction under ordinary conditions. It may, of course, be argued from the chemist's standpoint that atomic oxygen is itself in an excited and ephemeral state.

Spealman and the author were led, from some observations made on the nitrogen afterglow, to suspect that the reaction between nitric oxide and atomic oxygen was of this character. A simple experiment demonstrated that, when nitric oxide is mixed with atomic oxygen at low pressures, the reaction

$$NO + O = NO_2 \tag{1}$$

takes place accompanied by a greenish-white luminescence, which is of considerable intensity when approximately equivalent amounts of the reacting substances are present. This afterglow is not of sufficient intensity to photograph readily with a spectrograph of high dispersion, but when photographed with a Bausch and Lomb quartz spectrograph a series of diffuse, poorly resolved bands were obtained which extended throughout the visible spectrum with maximum intensity at about 5000 A.U. This spectrum appears to correspond to that observed by Strutt (Lord Rayleigh) (5), which has been designated by Stoddard (4) as the oxygen afterglow. The idea that nitric oxide was involved in the reaction producing this afterglow is, of course, not new. Strutt supposed that the reaction was between nitric oxide and ozone. When he attempted to prove this he was not able to get an afterglow with ozone made at atmospheric pressure, but he did get a chemiluminescent flash when nitric oxide was admitted to a trap in which ozone had been condensed with liquid air. Apparently Strutt did not realize that oxygen might be dissociated into atoms by the discharge at low pressures.[1]

The chemical proof that reaction 1 produces the luminescence is necessarily a process of elimination. There are a number of reactions possible between oxygen and the oxides of nitrogen, and an account of the study of these has been published elsewhere (3). It suffices to say that the reaction above is the only one that appears to take place, to an appreciable extent, under all circumstances in which the greenish-white afterglow is observed.

According to Mecke (1), nitrogen dioxide, when illuminated with light of wave length about 3700 A.U., decomposes by a predissociation process into nitric oxide and atomic oxygen, both species in the normal state. Reaction 1 therefore satisfies our criterion for a chemiluminescent reaction, viz., the formation of a molecule in an excited electronic state from atoms or molecules in the normal state. This process is not likely to take place in bimolecular collisions, of course, because the life of the complex is only the duration of the collision, which is very short compared to the time required for the emission of a photon. Accordingly, we must assume that

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[1] The whole matter has been confused by the publication of a note by Lord Rayleigh (Proc. Roy. Soc. London **150A,** 34 (1935)) in which he asserts that the ozone plus nitric oxide reaction produces the yellow afterglow characteristic of nearly pure nitrogen, and that oxygen containing no other impurity than water gives a white afterglow.

The yellow afterglow consists of the first positive bands of nitrogen, and this afterglow can be produced in nitrogen which contains no oxygen in any form. It is, of course, difficult to purify moist oxygen to a point where there is no afterglow, but it is possible to reduce the afterglow so much that it is scarcely visible in a darkened room, and one may suspect that this afterglow is due to traces of nitric oxide. It should be noted that the reaction between ozone and nitric oxide liberates only 48 calories of energy, which correspond to a short wave length limit of 5900 A.U.

reaction 1 takes place by triple collision with the loss of enough energy to stabilize the molecule. Provided further collisions do not occur within a period of 10^{-8} seconds, the residual excitation energy of the molecule will be radiated. At higher pressures this energy would probably be dissipated by collision, but it is, of course, difficult to produce atomic oxygen at higher pressures to test this prediction.

The varying amounts of energy lost in the triple collisions account for the widely distributed range of frequencies radiated. Were it not for this dissipation of energy, one would expect uniform radiation of wave length about 3700 A.U. The luminescence observed corresponds to the fluorescence observed by Norrish (2) when nitrogen dioxide is illuminated with light of wave length too short to produce dissociation. Nitrogen dioxide is a nonlinear molecule, and its absorption spectrum has not been analyzed. It is, therefore, not possible at present to identify the afterglow spectrum positively as belonging to nitrogen dioxide.

The duration of the afterglow is greatly decreased by increasing the pressure. At 1 mm. the afterglow disappears completely in about one second. This dependence upon pressure agrees with the hypothesis of triple collisions, although quantitative measurements are yet to be made.

The chemiluminescent efficiency of reaction 1 is probably quite high, but a large amount of energy is dissipated in the production of atomic oxygen. A more interesting property of the luminescence is that its spectral intensity distribution appears to approximate that of sunlight. Sufficient intensity has not been obtained, however, to make possible a test of its value as a source of illumination.

REFERENCES

(1) MECKE: Z. physik. Chem. **7B**, 108 (1930).
(2) NORRISH: J. Chem. Soc. **1929**, 1611.
(3) SPEALMAN AND RODEBUSH: J. Am. Chem. Soc. **57**, 1474 (1935).
(4) STODDARD: Proc. Roy. Soc. London **147A**, 464 (1934).
(5) STRUTT: Proc. Phys. Soc. London **23**, 66 (1910).

DISCUSSION

DR. OGG: Phenomena similar to that described by Professor Rodebush have been previously observed in the formation of diatomic molecules from atoms. Bonhoeffer and Pearson (Z. physik. Chem. **14B**, 1 (1931)) observed an intense emission of the band spectrum of OH molecules on mixing oxygen atoms and hydrogen atoms. Gaviola and Wood (Phil. Mag. [7] **6**, 1191 (1928)) similarly found an emission of the band spectrum of NH in a system containing nitrogen atoms and hydrogen atoms. The electronic band spectra of OH and NH molecules have been shown by

Bates (Z. physik. Chem., Bodenstein Festband, p. 329 (1931)) to be of the predissociation type. Since the electronic band spectrum of NO_2 also shows predissociation, it is probable that the emission of the NO_2 bands from oxygen atoms and NO molecules is a process entirely parallel to those cited.

PROFESSOR BATES: Professor Rodebush's results are in accord with the fluorescence of NO_2 observed by Norrish some years ago. He found that the fluorescence occurred only in those spectral regions where the quantum yield was less than the expected value of two.