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**The reaction of Sulfur Monoxide with Active
Nitrogen**

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Chimica. — *The reaction of Sulfur Monoxide with Active Nitrogen*^(*).
Nota di GIORGIO LIUTI^(**), presentata^(***) dal Corrisp. G. SARTORI.

RIASSUNTO. — Quando l'azoto attivo interagisce con una miscela di gas contenenti monossido di zolfo, viene osservata l'emissione di luce blu. L'analisi spettrale di questa emissione mostra che è simile all'emissione luminosa prodotta dalla reazione $\text{SO} + \text{O}(1)$. Il meccanismo più probabile comporta la reazione iniziale $\text{N} + \text{SO} \rightarrow \text{NO} + \text{S}(2)$ seguita da $\text{N} + \text{NO} \rightarrow \text{N}_2 + \text{O}(3)$ che genera gli atomi di ossigeno necessari per la (1).

INTRODUCTION.

Very little information is available in the literature on the reaction between active nitrogen and sulfur oxides. Previous studies, [1, 2], have indicated that SO_2 was not dissociated by active nitrogen. More recently, [3], it was suggested that a decomposition of SO_2 may take place under particular conditions. A blue luminescence was observed which was attributed to emissions from excited NO formed in the reaction between N and O atoms. Although no suggestion was given for the origin of the O atoms, it is possible that they could be formed by the dissociation of SO_2 following energy transfer from electronically excited nitrogen molecules, which are present in active nitrogen.

However, SO is also formed in the dissociation of SO_2 and the possibility that it partakes in a reaction with active nitrogen must be taken into account.

It is now known that the fastest reactions of N atoms are those with radicals or with molecules with a radical character in the ground state (that is having a total spin other than zero)⁽¹⁾. The most obvious example is the reaction with NO, which is generally used to titrate the N atoms. SO, which has a $\text{X}^3\Sigma$ as a ground state could react fast with N atoms. In a previous study, [4], a strong luminescence was found to occur when active nitrogen and a mixture of sulfur oxides was allowed to interact. Since SO can easily be produced and maintained for several milliseconds, especially at low pressure, it was decided to investigate such a reaction and the luminescence associated with it in the effort to understand the mechanism of the processes involved.

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(1) Because of the high multiplicity of the ground state N atoms, its reactions with radicals are the most likely to be spin allowed.

EXPERIMENTAL.

A conventional fast flow system was used in these experiments. The chemiluminescent reactions were studied in a quartz tube to allow optical observations in the ultraviolet. SO was produced either by passing O atoms, obtained from a discharge in pure O₂ or A—O₂ mixtures in a Woods Bonhoefer discharge tube, over solid sulfur located at one end of the quartz tube, as shown in fig. 1, or by discharging SO₂. Previous work, [4], showed that

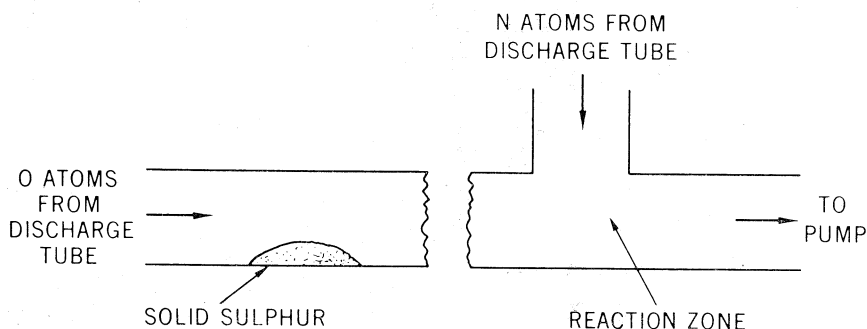


Fig. 1. — Schematic of the reaction tube.

in both cases a considerable concentration of SO could be obtained together with minor amounts of S₂O. Active nitrogen was produced in a second discharge and added at a point where all the chemiluminescent processes occurring upstream were completely absent. The N atoms concentration was measured by the usual NO titration method. A Hilger medium quartz spectrograph was used to analyze the light emission. The spectra were recorded on Kodak 103-F plates. The pressure for these experiments was 1 Torr. The gases were purified by use of dry ice or liquid O₂ traps. All experiments were performed at room temperature.

RESULTS AND DISCUSSION.

When the O atoms flowed over solid sulfur a blue glow appeared extending a few centimeters along the reaction tube. At the point of addition of active nitrogen a similar blue glow appeared again, lasting, as before only a few centimeters. After the completion of each run a small deposit of sulfur was found on the walls of the reaction tube at the interaction zone between active nitrogen and SO. Also, in some experiments a white afterglow similar to that resulting from the NO + O reaction was obtained. If, instead of active nitrogen O atoms were added, a much brighter blue glow was obtained. Under these conditions no sulfur deposit was found on the walls. When a discharge in SO₂ was used to produce SO, basically the same results were obtained. The glow in presence of active nitrogen had much lower intensity and size.

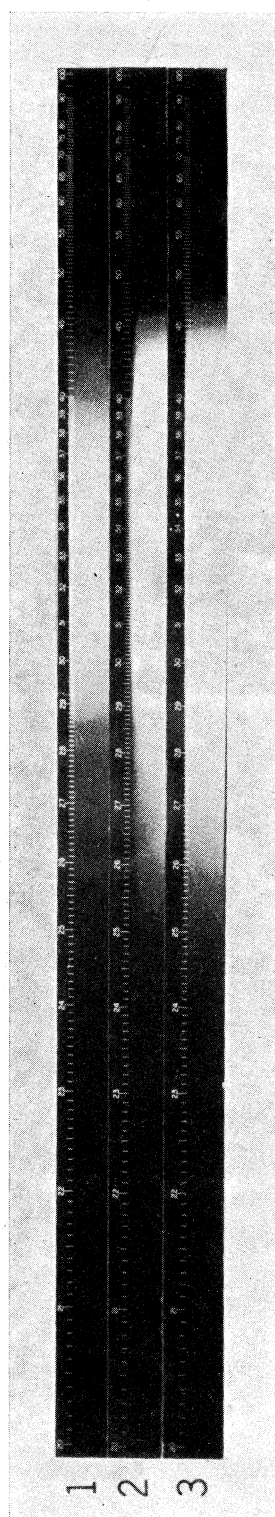


Fig. 2. — Spectra of the glows obtained in various conditions.

1. Glow from O atoms + sulfur.
2. Glow at the point of addition of active nitrogen.
3. Glow when O atoms are added instead of active nitrogen.

As before, sulfur was found deposited on the walls of the reaction tube. The white NO_2 afterglow was never observed in this case. In all cases the yellow nitrogen afterglow was completely destroyed. Fig. 2 shows the spectra taken under the various conditions described above (they refer to the experiments where SO was produced by the reaction of O atoms with solid sulfur). 1 is the spectrum of the glow obtained when O atoms react with sulfur, 2 is the spectrum of the glow at the point of active nitrogen, 3 is the spectrum of the glow obtained when O atoms are substituted for active nitrogen. The exposure time was five minutes for each spectrum. It is evident that the emissions are basically similar in all cases, the intensity being the only difference. No other emission other than the continuum in the blue and near ultraviolet is present. It appears that the same chemiluminescent reaction is responsible for the emissions observed. The reaction, as is now well known, [5-7] is:



Reaction (1) obviously occurs in cases 1 and 3 where O atoms are present in high concentration and can directly react with SO.

However, when active nitrogen is added, a fairly fast sequence of reactions must take place which is capable of generating O atoms, necessary for the occurrence of reaction (1), and sulfur.

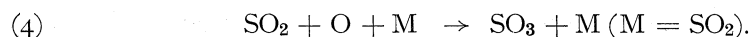
Under the conditions of these experiments the following mechanism can satisfactorily explain the major results:



However, here many complicating factors may intervene due to the presence of either molecular oxygen or SO_2 . For instance the N atoms could also react with O_2 present in large excess. This reaction provides an additional source of O atoms (and NO) and its net effect would be to increase the intensity of the glow.

The much lower intensity of the glow observed when SO_2 was the carrier gas can be attributed to the competition for the O atoms by the SO_2 itself.

SO_2 can undergo the three body process:



Reaction (4) has a rate constant at room temperature equal to $3 \times 10^{-32} \text{ cc}^2/\text{molec}^2 \text{ sec}$ [8]. Comparing the rate of formation of SO_3 through (4) with the rate of the chemiluminescent reaction ($k_1 = 7 \times 10^{-16} \text{ cc}/\text{molec sec}$, at room

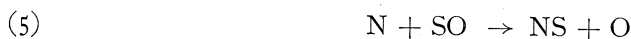
temperature [5]), the following is obtained:

$$(I) \quad + \frac{dSO_3}{dt} = k_4 [SO_2]^2 [O]$$

$$(II) \quad + \frac{dSO_2^*}{dt} = k_1 [SO] [O].$$

At a pressure of SO_2 of 1 Torr, and assuming a concentration of SO equal to about 1 % that of SO_2 a value of 10^2 is obtained for the ratio of I to II showing that (4) is indeed favored, even if the concentration of SO is higher than the value chosen above. The analogous reaction in presence of O_2 ($O + O_2 + M \rightarrow O_3 + M$) has a rate constant lower than the constant for reaction (4) by at least three orders of magnitude. As a consequence in the latter case at the same pressure the chemiluminescent reaction is predominant.

The reaction could also follow the primary path:



(2) and (3) and (5) and (6) are indistinguishable in these experiments. Although the net result is the same, it seems unlikely that (5) and (6) occur to a great extent because they do not produce NO whose presence is strongly suggested by the white NO_2 afterglow observed in some of the experiments.

S_2O , which is also present with SO, could react with N atoms yielding SO and NS. It should be mentioned that it was found, [9], that in presence of O atoms S_2O rapidly decomposes into two SO molecules. It is, therefore, possible that S_2O plays only a minor role.

Also the formation of a sulfur deposit, even in presence of O_2 , rules out the reaction:



which, in any case, would favor the occurring of (1). N_2 electronically excited, in either the $B^3\Pi$ state or the $A^3\Sigma$ state which seems to be very important in initiating reactions of active nitrogen in cases where the N atoms react slowly, [10], should not play a major role here. The relatively high rate of consumption of N atoms, as indicated by the complete disappearance of the yellow N_2 afterglow, makes their reactions predominant over any other process involving species in much lower concentration such as N_2^* .

It seems therefore, that reaction (2) is indeed occurring and initiates the processes which lead to the observed luminescence. No precise information can be obtained about its rate constant from these experiments. A value could be accurately measured in conditions where interference from secondary reactions is reduced to a minimum. This possibility is now being investigated.

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