

## Preliminary Note

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### Chemiluminescence in the gas-phase reactions of ozone with cyanoacetylene, carbon disulfide and thiophene\*

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Many gas phase reactions of ozone produce electronically excited states which give rise to well characterized spectra that are of considerable current interest [1 - 3]. Reported here are three new chemiluminescent ozone systems, measured with apparatus previously described [1]. The spectra were obtained at room temperature using a Jarrell-Ash 0.25 m monochromator with a spectral slit width of 3 nm and a cooled EMI 9683QKB photomultiplier. The ozone from a discharge through oxygen was adsorbed on silica gel at  $-78^{\circ}\text{C}$  and eluted with a helium or oxygen carrier at a total pressure of approximately 50 Torr. Ozone and substrate pressures were approximately 1 Torr each. Cyanoacetylene (from Farchan Research Laboratories, Willoughby, Ohio) carbon disulfide (Fisher Scientific Co., Research Grade) and thiophene (Aldrich Chemical Co., Gold label) were all vacuum distilled before use.

The total intensities uncorrected for spectral response and relative to ethylene = 1 were as follows: cyanoacetylene, 22; carbon disulfide, 540; thiophene, 60.

#### *O<sub>3</sub> + cyanoacetylene*

Although cyanoacetylene ( $\text{HC}_3\text{N}$ ) was described in 1920 [4] it has only recently become widely known as a result of being detected in interstellar space [5]. The uncorrected chemiluminescent spectrum is shown in Fig. 1 and the main features can be identified as follows [6]. The bands at 788 and 693 nm are from the red CN system and are due to the  $\text{A}^2\Pi \rightarrow \text{X}^2\Sigma$  transition with  $\Delta\nu = 2$  and  $\Delta\nu = 3$ , respectively. The violet CN bands ( $\text{B}^2\Sigma \rightarrow \text{A}^2\Pi$ ) give peaks at 456 nm ( $\Delta\nu = 2$ ), 418 nm ( $\Delta\nu = 1$ ) and 385 nm ( $\Delta\nu = 0$ ). There are in addition numerous partly resolved peaks from the red and violet CN bands. The largest peak in Fig. 1 is at 432 nm and is due to  $\text{CH}(\text{A}^2\Delta \rightarrow \text{X}^2\Pi, \Delta\nu = 0)$ .

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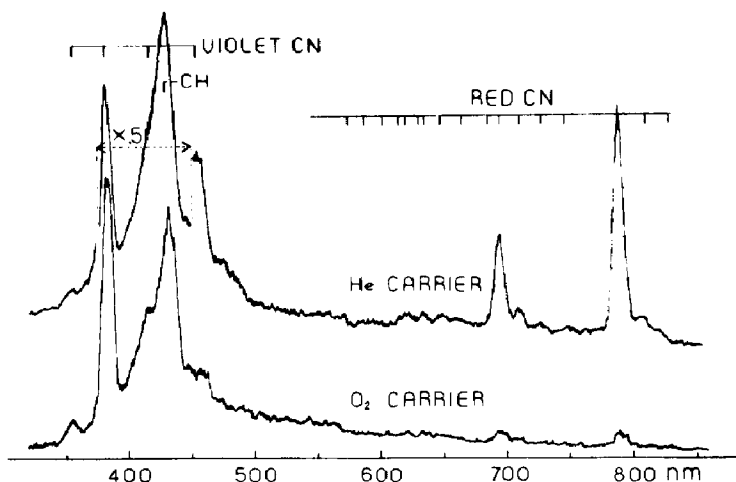


Fig. 1. Emission from ozone with cyanoacetylene.

The attack of  $O_3$  on  $HC\equiv C-C\equiv N$  is clearly at both triple bonds to give fragments from both ends of the molecule. The production of  $CH(^2\Delta)$  has been noted in the reaction of  $O_3$  with acetylene [2, 7] and with allene [2, 8]. We know of no reported work on the luminescence from  $O_3 +$  cyanides but in a recent study [9]  $HC_3N$  was photolyzed in the vacuum ultra-violet to form  $CN(X^2\Sigma)$  which was then excited by a dye laser to form  $CN(B^2\Sigma)$ . The resulting fluorescence gave 0-0, 1-1 and 2-2 bands. Similar results were obtained in the photolysis of  $ICN$  [10].

The effect of an  $O_2$  carrier on the  $O_3 + HC_3N$  chemiluminescence is shown in Fig. 1. The  $CH$  band is little affected which is to be expected since this species is a common emitter in hydrocarbon oxidation. The violet  $CN$  bands are also little quenched by  $O_2$  but the red  $CN$  bands are barely seen, suggesting the precursor reacts readily with  $O_2$ .

#### $O_3 +$ carbon disulfide

The chemiluminescence from  $O_3 + CS_2$  is shown in Fig. 2 and consists of a structureless band with a maximum at  $\sim 365$  nm and a short wavelength cutoff at  $\sim 280$  nm. This band is identical with that seen from the reaction of  $O_3$  with  $H_2S$ ,  $CH_3SH$  and  $(CH_3)_2S$  [11, 12] and which has been shown by Pitts *et al.* [11] to arise from  $SO + O_3 \rightarrow O_2 + SO_2(^1B_1) + 106$  kcal/mol. The kinetics of the reaction between  $O_3$  and  $CS_2$  have been studied by Olszyna and Heicklen [13] who have postulated that the  $SO$  radicals arise from oxygen atoms, produced by ozone decomposition, reacting as follows:  $O + CS_2 \rightarrow CS + SO$ .

#### $O_3 +$ thiophene

The emission from  $O_3 + C_4H_4S$  is shown in Fig. 3 and has two well-defined features. The structureless band is from singlet excited  $SO_2$ , as for the  $O_3 +$  carbon disulfide system. The source of  $SO_2(^1B_1)$  is probably as

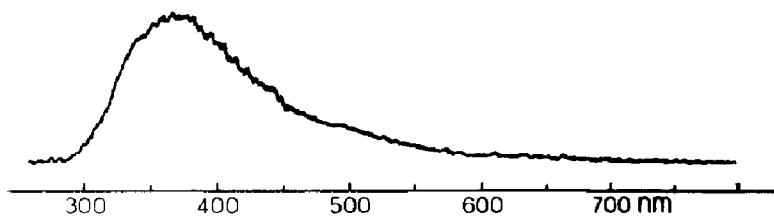


Fig. 2. Emission from ozone with carbon disulfide using He carrier.

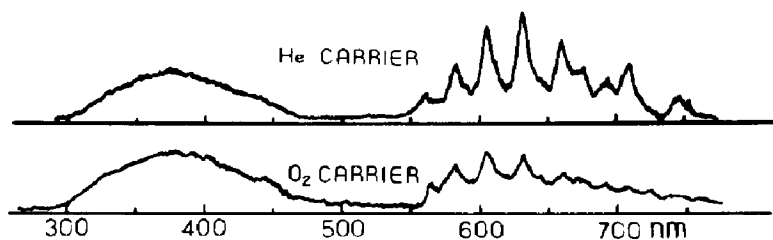


Fig. 3. Emission from ozone with thiophene.

discussed previously but other possibilities are  $\text{CS}(^1\Sigma) + \text{O}_3 \rightarrow \text{CO} + \text{SO}_2(^1\text{B}_1) + 189 \text{ kcal/mol}$  or  $\text{HS}(^2\Pi) + \text{O}_3 \rightarrow \text{OH} + \text{SO}_2(^1\text{B}_1) + 131 \text{ kcal/mol}$ . However, the short wavelength cutoff corresponding to  $\sim 102 \text{ kcal/mol}$  suggests SO as the precursor.

The other feature from the  $\text{O}_3 + \text{thiophene}$  emission is a banded structure extending from 500 to 825 nm. The bands are identical with those observed by Becker *et al.* [12] in the reaction between  $\text{O}_3$  and hydrogen sulfide. They ascribed the emission as due to the electronically excited HSO radical from the reaction  $\text{SH} + \text{O}_3 \rightarrow \text{HSO} + \text{O}_2$ . They found no quenching effect of  $\text{O}_2$  on  $\text{SO}_2$  or HSO emissions. As seen in Fig. 3, we find  $\text{O}_2$  does not quench the  $\text{SO}_2$  emission but does reduce the HSO intensity, suggesting that  $\text{O}_2$  reacts with a precursor. This parallels the observation that added  $\text{O}_2$  has no effect on the rate of the reaction between  $\text{O}_3$  and  $\text{H}_2\text{S}$  [14] but slows the reaction between  $\text{O}_3$  and thiophene [15].

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