

Table I

Reactant	Relative integrated emission intensity <sup>a</sup>
Ethylene	1
Trimethylethylene	50
Tetramethylethylene	50
<i>Cis</i> -or <i>trans</i> -butene-2	10 <sup>b</sup>
2,3-Dimethylbutadiene	8 <sup>b</sup>
2,5-Dimethyl-2,4-hexadiene	30 <sup>b</sup>
Hydrogen sulfide	25
Dimethyl sulfide	200
Methanethiol	2000 <sup>b</sup>
2,5-Dimethylfuran	40 <sup>b</sup>

<sup>a</sup> Relative to ethylene = 1.

<sup>b</sup> Preliminary experiments. No spectra presented.

widths of about 10 nm and appear unstructured at the slit widths employed.

Table I presents a comparison of the intensities of the emissions from the reactions of ozone with those compounds whose spectra have been discussed and with a number of other compounds which have been investigated in preliminary experiments.

Surprisingly, ethylene, the compound presently used in homogeneous gas-phase chemiluminescent ozone detectors (Warren and Babcock, 1970), has the lowest integrated emission intensity of all the compounds examined to date.

#### Discussion

It is not our purpose at this time to try to elucidate the nature of the luminescing species in these reactions or to speculate about possible mechanisms of their formation. Nevertheless, on the basis of previous work (Cadle and Ledford, 1966; Cullis and Roselaar, 1959; Sharma et al., 1965), it seems likely that electronically excited SO<sub>2</sub> is the source of the luminescence in the reactions of ozone with hydrogen sulfide and dimethylsulfide. The nature of the emitting species in the ozone-olefin reactions cannot be definitely established at this time, although it is likely that de-excitation of the carbonyl functional group is involved. On the basis of product analysis, contributions to the integrated emission intensity due to excited formaldehyde or acetaldehyde are possible in the ethylene-ozone system (Vrbaski and Cvetanovic, 1960; Scott et al., 1957), whereas contributions due to excited ace-

tone, acetaldehyde, and possibly  $\alpha$ -dicarbonyl products are possible in the trimethylethylene- and tetramethylethylene-ozone systems (Vrbaski and Cvetanovic, 1960). Further work is underway in this laboratory to elucidate the mechanisms of these reactions.

The importance of the results presented in this paper lies first in the observation that a number of compounds yield electronically excited ozonolysis products which exhibit quite large integrated emission intensities relative to ethylene. Ethylene-ozone reactions have already been used successfully in the continuous monitoring of ozone in the sub-part-per-million concentration range (Warren and Babcock, 1970). It is obvious, therefore, that the use of compounds such as those listed in Table I instead of ethylene could very well result in a greatly increased sensitivity of this method. Furthermore, it may also be feasible to determine quantitatively trace amounts of sulfur-containing pollutants by means of their chemiluminescent reactions with ozone.

Also, these studies provide direct evidence that, at least in the mm pressure range, electronically excited species are produced in many gas-phase ozone-olefin reactions. This observation may be of considerable importance in understanding the detailed mechanisms of the formation of photochemical smog.

#### Acknowledgment

The authors acknowledge the support of this research by a grant of Themis N 00014-69-A-0200-500 and by grants AP-00109 and AP00771, Research Grants Branch, Air Pollution Control Office, Environmental Protection Agency.

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Received for review December 7, 1970. Accepted February 26, 1971.

#### CORRECTION

##### EFFECT OF PEROXYACETYL NITRATE (PAN) IN VIVO ON TOBACCO LEAF POLYSACCHARIDE SYNTHETIC PATHWAY ENZYMES

In Table III of this article by L. Ordin, M. J. Garber, J. I. Kindinger, S. A. Whitmore, L. C. Greve, and O. C. Taylor [ENVIRON. SCI. TECHNOL. **5** (7), 625 (1971)], add a footnote *e* at the intersection of the column headed "NaOH-Sol, Base" with the row title "Simple effects."