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SPECIFIC METHOD FOR THE DETERMINATION OF OZONE IN THE ATMOSPHERE

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16. Abstracts *A description is given of work undertaken to develop a simple, specific, and reliable method for ozone. Reactions of ozone with several 1-alkenes were studied at room temperature (25°). Eugenol (4-Allyl-2-methoxy phenol), when reacted with ozone, was found to produce relatively large amounts of formaldehyde as compared to other 1-alkenes tested. The method described was compared with alkaline iodide method for the determination of various concentrations of ozone in the range of 0.05 to 2.0 ppm. The reactions of ozone with eugenol were found to yield stoichiometric amounts of formaldehyde. Hydrogen peroxide, peracetic acid, sulfur dioxide and various reducing agents commonly present in the air, do not interfere with the method. Formaldehyde when present in the air, must be determined simultaneously and the concentration of formaldehyde subtracted from that of the ozone. Any formaldehyde monitoring equipment can be easily adopted for the determination of ozone.*

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SPECIFIC METHOD FOR THE DETERMINATION OF OZONE IN THE ATMOSPHERE

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Ozone is the principal oxidant in the photochemical smog, and a detailed study of ozone toxicity in man has been reported by Griswold, et al. (Griswold, 1957). It is also considered to be the most damaging of all air pollutants affecting vegetation (Heggestad, 1969). The natural occurence of ozone and its formation in the urban atmospheres is well known (Renzetti, 1959).

Published methods for the determination of ozone involve a variety of analytical techniques such as chemical oxidation (Brewer and Milford, 1960; Byers and Saltzman, 1959; Haagen-Smit and Brunelle, 1958; Saltzman and Gilbert, 1959), absorption of ultraviolet light (Cohen, et al., 1967; Renzetti and Romanowsky, 1959; Stair, et al., 1954), catalytic decomposition (McCully, et al., 1961; Olmer, 1959), chemiluminescence or fluorescence (Regner, 1960; Watanbe and Nakodoi, 1966), and cleavage of an olefinic bond (Bradley and Haagen-Smit, 1951; Bravo and Lodge, 1964; Bufalini, 1968; Hauser and Bradley, 1966). Most of these methods are not specific for ozone, and they are generally used for determinations of total oxidants. Others which are specific suffer the disadvantage that they are very complicated or require frequent calibration. Obviously the need for a simple, specific, and reliable method for ozone is becoming critical.

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The method presented here is based on the reaction of ozone with 4-allyl-2-methoxy phenol (eugenol). This reaction has been found to be specific. Moreover, the stoichiometry of the reaction involves the formation of one molecule of formaldehyde for each molecule of ozone consumed. Formaldehyde formed is determined by a slight modification of the West-Gaeke procedure (1965) for sulfur dioxide.

EXPERIMENTAL

APPARATUS:

Gas samplers (described by Wartburg, Pate and Lodge, 1969), midget impingers (MSA Catalog No. 46984).

Air flow meters (Fisher and Porter Co., Catalog No. 450-015).

Dyna-vac pump (Cole-Parmer, Catalog No. 7064).

Beckman D B spectrophotometer

REAGENTS:

Para-rosaniline hydrochloride (Fisher Scientific Co., Catalog No. 42500).

Mercuric chloride, sodium chloride, sodium hydroxide, potassium iodide, sulfamic acid and standard formaldehyde solution (1000 mg/l).

Sodium tetrachloromercurate(II) solution: This solution was prepared by dissolving 13.6 g of mercuric chloride and 5.8 g of sodium chloride per liter of distilled water.

Para-rosaniline reagent:

Prepared by dissolving 0.16 g of para-rosaniline hydrochloric in 24 ml of concentrated HCl, then diluting to 100 ml with distilled water.

Alkaline iodide solution:

Ten grams of KI and 40 g of NaOH were dissolved per liter of water.

Acidifying reagent:

Five grams of sulfamic acid were dissolved in 100 ml of water, then 84 ml of 85% phosphoric acid were added and the mixture was made up to 200 ml.

Preparation of ozonized air:

Samples of ozonized air were prepared by passing prepurified air through a brown glass aspirator bottle of 5 liter capacity in which a germicidal lamp (4 Watt, General Electric) was fixed. The mouth of the bottle was sealed with a cork through which passed the leads of the lamp and an outlet tube as shown in Figure I. After initial assembly of the ozonation apparatus, the lamp was kept on for a week so that it could generate enough ozone to react with any of the organic matter that might be present in the aspirator. Subsequently, before analyses, the lamp was turned on every morning at least an hour before any samples were ozonized. Ozone concentrations could be established at any desired concentration between 0.5 and 10 ppm by adjusting the flow of air through the aspirator. Lower concentrations (down to 0.05 ppm O_3) were obtained by partially covering the lamp with aluminum foil and equilibrating the system for ten days to allow for any reaction of ozone with aluminum foil.

Sampling Procedure:

The sampling equipment was set up as shown in Figure I. The gas samplers shown were obtained from the National Center for Atmospheric Research, Boulder, Colorado. Alternatively, midget impingers were also found to be satisfactory. Two sampling bubblers were used in series. One was used as an impinger in which air containing ozone was directed upon the surface of eugenol

placed in the container; the second, containing 10 ml of distilled water, was used as an absorber for formaldehyde. Air in the first impinger was passed through an orifice of 1 mm diameter at a rate of 2 l/m. The jet velocity has been estimated to be 44 m/sec. With 1 ml of eugenol in the tube, the spacing between the orifice tip and the surface of the eugenol was 5 mm. In the second bubbler the orifice may be replaced by a frit which must be completely immersed in the water used for absorbing the formaldehyde.

Purification of eugenol:

Eugenol, as well as all other 1-alkenes tried, was found to contain formaldehyde as an impurity, probably this results from the exposure of the compounds to atmospheric ozone. Each olefin was purified just before use, by passing it through a 3 inch colume of pure, dry sodium sulfite crystals.

RESULTS AND DISCUSSION

A study of ozonolysis of various 1-alkenes was undertaken to develop a reliable method for the determination of ozone. A similar attempt was made by Hauser and Bradley (1966) who reacted ozone with various 1-alkenes directly in solvents such as ethyl acetate, acetic acid, dimethyl sulfoxide, etc. They found formaldehyde in some of the ozonized mixtures but discontinued studies along this line because of water insolubility of 1-alkenes and high degree of color formed in the blank determinations.

Because of the high reactivity of ozone, it was decided that the direct passage of ozone-containing air samples into 1-alkenes and then through a second bubbler containing 10 ml of distilled water would be the most reliable approach. The formaldehyde, which has a low boiling point (-21°C) and a very low solubility in alkenes, was expected to be collected in the second bubbler. Air containing known concentrations of ozone was reacted with several organic compounds containing the $-CH = CH_2$ group and the formaldehyde formed

was collected and determined by the metho. of Lyles et al., (1965). The results are shown in Table I. Impinging of air on the alkene was found to be as effective as bubbling for the production of formaldehyde. In the case of bubbling, however, more alkenes were carried out over the second container and had to be removed before taking final spectrophotometric readings.

Determination of formaldehyde:

Two reliable methods are available for the determination of formaldehyde: (1) The method developed by Lyles, et al., (1965) and (2) The chromotropic acid method (West, et al., 1956; Altshuller, et. al., 1961). The latter method was found unsuitable because some vapors of eugenol were carried into the air along with the formaldehyde formed and interfered. The method of Lyles, et al., which is based on a slight modification of the West-Gaeke method for sulfur dioxide, has been found to be simple, reliable, and satisfactory for the determination of formaldehyde formed by the reaction of ozone and eugenol.

Stoichiometry of the reaction:

The ozone concentration in an air containing about 2 ppm. of ozone was determined by the formaldehyde method, the neutral iodide method and the alkaline iodide method. The same ozonized air under exactly similar conditions was used in all three determinations. The following results were obtained:

Method	Ozone Concentration(ppm)
Neutral iodide	2.3
Alkaline iodide	1.55
Eugenol-formaldehyde	1.50

A recent report on the stoichiometry of the iodide method, by Boyd, et al., (1970), indicated that the alkaline iodide method yields one iodine molecule for every molecule of ozone reacted, whereas the neutral iodide method actually yields 1.54 molecules of iodine per molecule of ozone reacted. Results of the present study are in complete agreement with the results of Boyd, et al., although our method for the determination of ozone is completely different.

Determinations of ozone at different concentration levels:

Ozone was determined in several samples of air containing ozone in the range of 0.05 to 2.0 ppm. Each concentration level was determined three times by the alkaline iodide method as well as by the eugenol-formaldehyde procedure. Results are given in Table II.

The eugenol-formaldehyde method yields results comparable to those obtained by the alkaline iodide method of Byers and Saltzman (1959), at all concentrations within the range of (0.05 to 2 ppm). Since it is unlikely that ozone will exist in ordinary atmospheres at concentrations greater than 2.0 ppm, determinations of higher concentrations were not extensively investigated. A few concentrations in the range of 2-5 ppm of ozone were determined by the eugenol-formaldehyde procedure, but no comparison was made with the iodide method.

Sensitivity of the method:

The sensitivity of the method is exactly the same as that for the formaldehyde method of Lyles, et al., (1965), since ozone reacts to produce formaldehyde in a 1/1 mole ratio. An ozone concentration of 0.02 ppm can be easily determined by sampling the air for 40 minutes at a rate of two liters per minute.

Selectivity of the method:

The eugenol-formaldehyde method described seems to be specific for ozone.

However, it is important that appropriate correction be made for the formaldehyde present in the ambient atmosphere. This presents no problem because the formaldehyde background level can be determined as a check by simply by-passing the first (eugenol) impinger and collecting and determining the formaldehyde in a separate bubbler.

Interference effects of hydrogen peroxide (3%) and peracetic acid were examined by spraying the two solutions into the air being sampled. Neither of these compounds produced any formaldehyde when reacted with eugenol. Sulfur dioxide and other reducing agents present in the air were not observed to interfere with the ozone determination.

Field studies:

The method has been tested for on-site determinations of ozone. These studies indicate that the method would be quite suitable for field studies (Lyles, 1970). Any formaldehyde monitoring equipment can be easily adapted for monitoring ozone. One need only connect to the formaldehyde monitor a midget impinger containing 1 ml of eugenol to convert it to an ozone monitor.

ABSTRACT

A simple, sensitive and specific method for the determination of ozone in the atmosphere is described. Reactions of ozone with several 1-alkenes were studied at room temperature (25°). Eugenol (4-Allyl-2-methoxy phenol), when reacted with ozone, was found to produce relatively large amounts of formaldehyde as compared to other 1-alkenes tested. The method described was compared with alkaline iodide method for the determination of various concentrations of ozone in the range of 0.05 to 2.0 ppm. The reactionsof ozone with eugenol were found to yield stoichiometric amounts of formaldehyde. Hydrogen peroxide, peracetic acid, sulfur dioxide and various reducing agents commonly present in the air, do not interfer with the method. Formaldehyde when present in the air, must be determined simultaneously and the concentration of formaldehyde subtracted from that of the ozone. Any formaldehyde monitoring equipment can be easily adopted for the determination of ozone.

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TABLE I

STUDY OF OZONOLYSIS OF VARIOUS 1-ALKENES

Sampling Rate --- 2 l/mn.
Sampling Time --- 5 mn.

Ozone concentration determined by neutral iodide method --- 2.2. ppm
Ozone concentration determined by alkaline iodide method --- 1.5 ppm

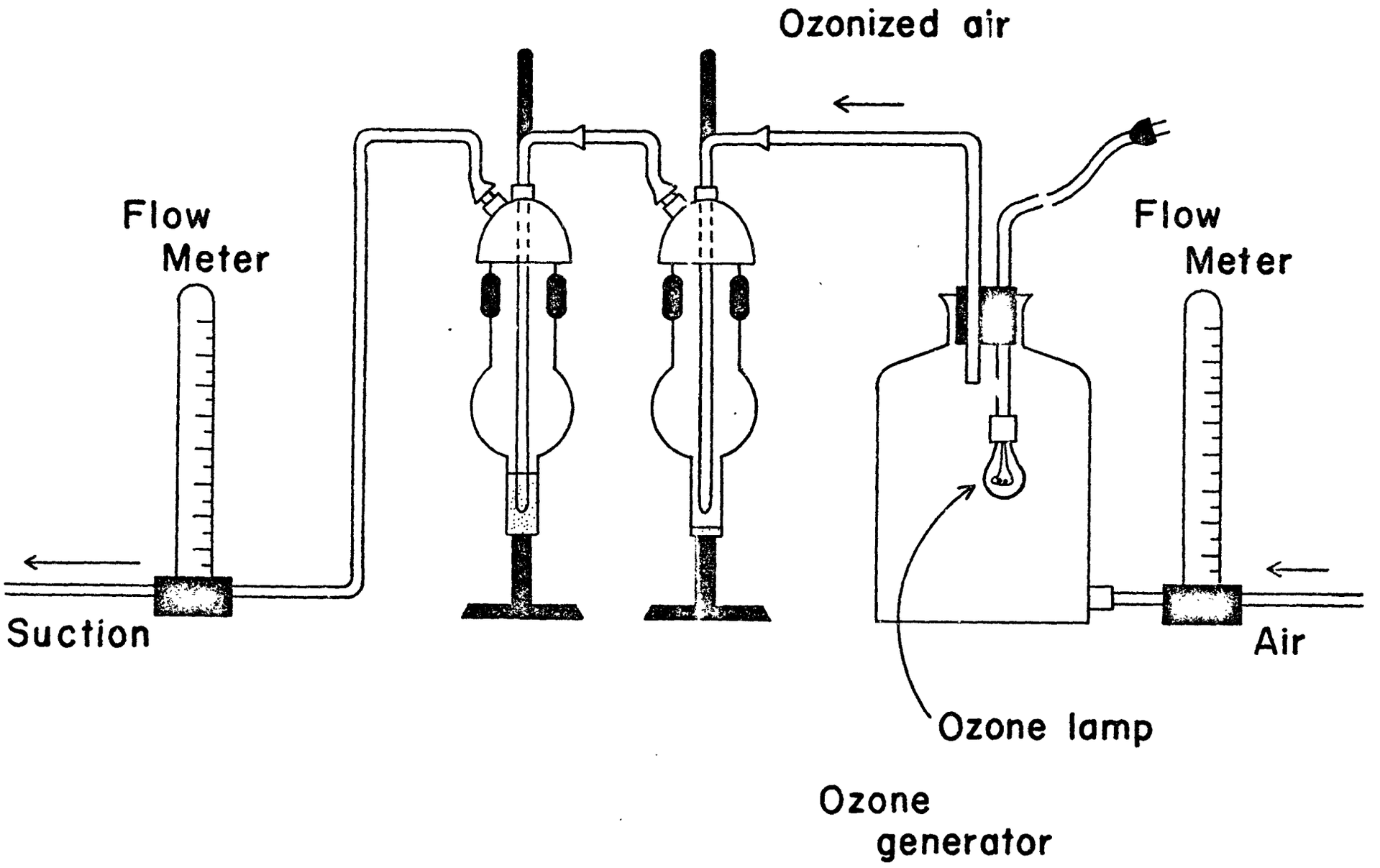
Compound Used	HCHO obtained(μg)	Ozone Concentration (Proposed Method PPM)
1-Octene	9	0.67
1-Decene	9	0.67
1-Dodecene	8	0.60
Eugenol	20	1.5
3,4 Dimethoxyallyl benzene	6	0.45
Diallyl phthalate	6	0.45
Diallyl isophthalate	6.5	0.49

TABLE II

Comparative Study of Eugenol-formaldehyde method and Alkaline iodide method.

Ozone Concentration (ppm)*	
Alkaline iodide method	Eugenol-formaldehyde Method
0.045	0.050
0.11	0.10
0.18	0.17
0.25	0.25
0.99	0.92
1.20	1.15
1.50	1.45
1.90	1.80

*Results tabulated are averages of three samples.


Ozonized air
Flow
Meter
Flow
Meter
Suction
Air
Ozone lamp
Ozone
generator