CHEMISTRY LETTERS, pp. 1287-1290, 1993.

Production of Hydrogen Peroxide and Organic Hydroperoxides in the Reactions of Ozone with Natural Hydrocarbons in Air

Shiro HATAKEYAMA,* Haiping LAI,† Shidong GAO,†† and Kentaro MURANO
Global Environment Division, National Institute for Environmental Studies,
Tsukuba, Ibaraki 305

Reaction of ozone with three kinds of olefins in air was studied. H_2O_2, CH_3OOH, and $HOCH_2OOH$ were collected and analyzed with HPLC with a fluorometric detector. Direct reaction of CH_2OO with H_2O was found to be the source of $HOCH_2OOH$. CH_3OOH was formed only from the olefins which have a methyl group. Detailed reaction mechanisms are discussed.

Recently the new-type forest decline found in Europe or North America, e.g., so-called "Waldschäden", has been ascribed to atmospheric oxidants including ozone and hydrogen peroxide.[1,2] In addition, formation of organic peroxides such as hydroxymethyl hydroperoxide (HMHP, $HOCH_2OOH$), methyl hydroperoxide (MHP, CH_3OOH), bis(hydroxymethyl)peroxide (BHMP, $HOCH_2OOCH_2OH$), and so on were reported.[3,4] Hewitt et al.[5] found that hydroperoxides (ROOH) were formed in the leaves of plants exposed to ozone. Recently, Hewitt and Terry[6] pointed out that damage to lipids via ROOH formation would be possibly more extensive than that caused by direct reaction with ozone.

Previously reported yields of peroxides from ozone-alkene reactions are quite scattered and the formation mechanism is unclear so far.

In the work reported here we studied ozone-alkene reactions employing 4 m^3 photochemical reaction chamber to conduct experiments in ppmv range. The details of the chamber were already reported.[7] After the chamber was filled with purified air up to 105 kPa, ozone was introduced into the chamber (~1 ppmv). The concentration of ozone was monitored with a chemiluminescent ozone analyzer. Then, one of reactant alkenes was measured volumetrically and introduced into the chamber (~3 ppmv) with a stream of pure nitrogen. The concentration of alkenes was measured every 5 min by means of a gas chromatograph with a flame ionization detector.

Studied alkenes were isoprene (Wako), 1-methylcyclohexene (Wako), and methylenecyclohexane (Aldrich) and used after degassing. 1-Methylcyclohexene and methylenecy-

---

† On study leave from Tokyo University of Agriculture and Technology.

†† Research fellow supported by International Good Neighborhood Association, Japan. Present address: Chongqing Institute of Environmental Science and Monitoring.

clohexane were used as model compounds of α-pinene and β-pinene, respectively. We have already reported that 1-methylcyclohexene and methylenecyclohexane reacts with ozone quite similarly to α- and β-pinene, respectively.[8)]

Products were collected by use of a mist chamber[9)] with water or dilute phosphoric acid (pH ~3.5), and subjected to analysis by means of a high performance liquid chromatograph (HPLC) equipped with a fluorescence detector. Polymer column and tubing were used to eliminate decomposition of hydroperoxides on metal surfaces. Separation column was 5 μm ODS-2. To minimize decomposition of peroxides in the column, the column was cooled at 1 °C. Analyzing conditions were as follows. Mobile phase: diluted H_3PO_4, pH3.5, 0.5 mL/min. Buffer: 0.01 mol/L KH_2PO_4/NaOH, pH9.4, 0.2 mL/min. Reagent: 0.5 mg of p-hydroxyphenylacetic acid (Wako) and 2 mg of horseradish peroxidase (Sigma, EC 1.11.1.7, 310 U/mg) in 100 mL of 0.01 mol/L KH_2PO_4. All solutions were prepared with water deionized, distilled, and distilled again from manganese oxide.

For calibration, MHP was prepared according to the method described by Vaghjiani and Ravishankara.[10)] Identification of HMHP was attained by monitoring the decomposition of BHMP. BHMP was prepared by Marklund's method.[11)] It decomposed to HMHP and H_2O_2 gradually as reported by Marklund[11)] in dilute phosphoric acid at pH=3.5.

Figures 1a, b, and c are chromatograms of the products formed by the reaction of ozone with isoprene, 1-methylcyclohexene, and methylenecyclohexane, respectively. As shown in Fig. 1a, isoprene yielded H_2O_2, HMHP, and MHP as major peroxidic products. Some unidentified peaks in the chromatogram were observed. 1-Methylcyclohexene gave H_2O_2 and MHP, mainly, with a very small amount of HMHP. From methylenecyclohexane H_2O_2 and HMHP were produced. The yields are listed in Table 1. All the yields

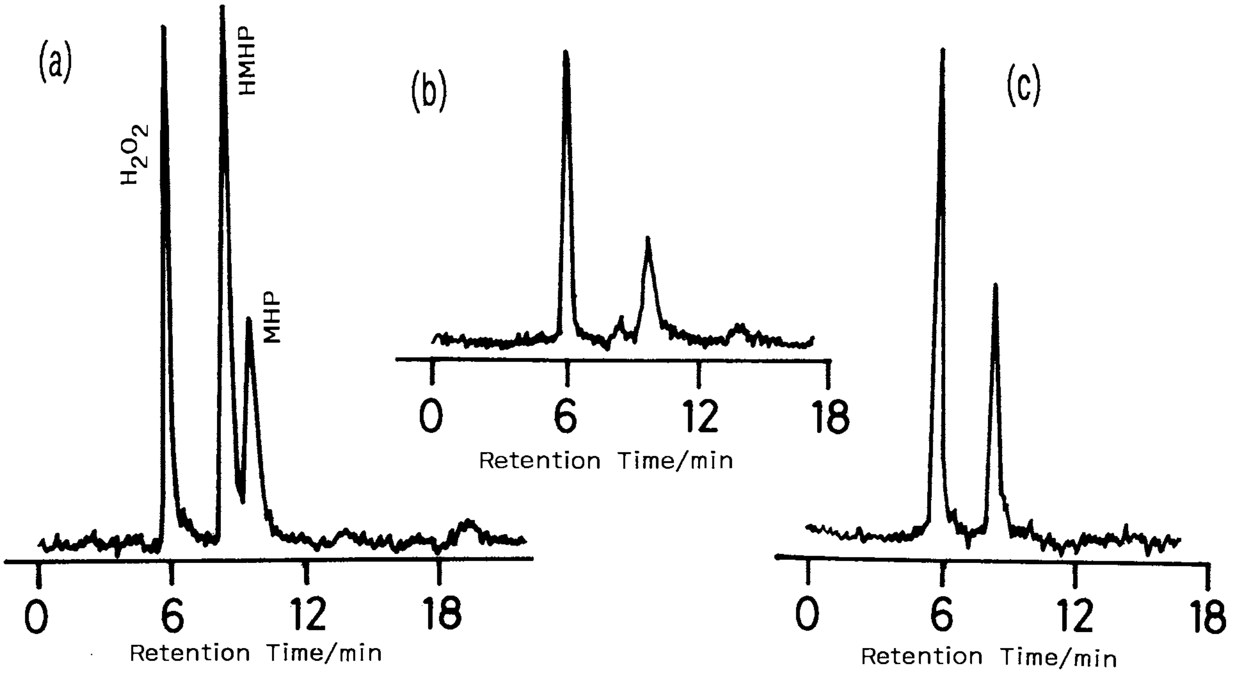


Fig. 1. Chromatograms of the products of the reactions of ozone with isoprene (a), 1-methylcyclohexene (b), and methylenecyclohexane (c).

cited were measured after ozone was consumed to avoid the contribution of liquid phase formation of hydrogen peroxide during the sampling of ozone-containing air.

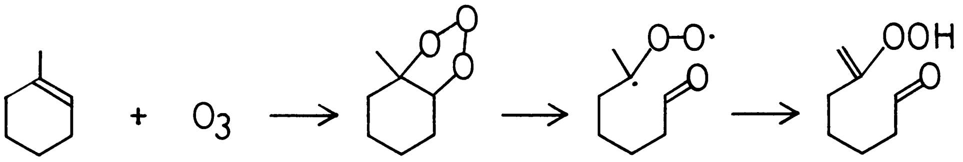
Table 1. Yields of peroxides in the reactions of ozone with isoprene, 1-methylcyclohexene, and methylenecyclohexane

Alkene	Sample No.	$[\text{Alkene}]_0$	$[\text{Ozone}]_0$	RH/%	Average Yield/%		
					H_2O_2	HMHP	MHP
Isoprene	4	2.3-3.7	0.6-1.0	0	0.85	2.8	1.9
	1	3.9	0.75	20	3.6	3.3	2.7
1-Methyl-cyclohexene	5	2.1-3.7	0.5-1.1	0	1.2	<0.01	1.7
	2	2.1-3.5	0.8-1.0	10-13	1.6	0.02	1.6
Methylene-cyclohexane	4	2.2-3.6	0.5-1.0	0	0.47	0.44	-
	2	3.5-3.6	0.6-0.8	10-17	1.3	3.0	-

Formation of the above products can be explained as follows. The reaction of the Criegee intermediate (CH_2OO biradical) with water gives HMHP. Even in dry air some water vapor is still contained (≤ 1 ppmv). Thus, the water vapor can react with some highly reactive radicals such as the Criegee intermediates. In the cases of isoprene and methylenecyclohexane formation of both H_2O_2 and HMHP were enhanced very much in humid air. That indicates the participation of water to the reaction. We have reported that the Criegee intermediate can react with water to give formic acid via hot HMHP (Reaction 4a).12) The result of this study shows that the hot HMHP thus formed is stabilized (Reaction 4b) to some extent. MHP is formed by the reaction of CH_3OO radical with HO_2 radical (Reaction 5-6).

$$O_3 + \text{isoprene} \rightarrow CH_2OO + HCHO + CH_3 + \text{other products} \quad (1)$$
$$O_3 + \text{1-methylcyclohexene} \rightarrow CH_3 + \text{other products} \quad (2)$$
$$O_3 + \text{methylenecyclohexane} \rightarrow CH_2OO + HCHO + \text{other products} \quad (3)$$
$$CH_2OO + H_2O \rightarrow HOCH_2OOH^{\ddagger} \rightarrow HCOOH + H_2O \quad (4a)$$
$$\rightarrow \text{HMHP} \quad (4b)$$
$$CH_3 + O_2 \rightarrow CH_3OO \quad (5)$$
$$CH_3OO + HO_2 \rightarrow CH_3OOH + O_2 \quad (6)$$

Since methylenecyclohexane has no methyl group, no MHP was formed. 1-Methylcyclohexene does not have a terminal methylene group, it cannot form CH_2OO directly. Thus, the yield of HMHP from 1-methylcyclohexene was quite low. However, if following hydroperoxyalkene formation takes place as reported by Niki et al.13) for the reaction of ozone with fully substituted alkenes, there is a possibility that CH_2OO is formed as a secondary product. Since isoprene has not only a methyl group but also terminal methylene groups, both HMHP and MHP were formed.



(7)

Recently Simonaitis et al.[14] and Becker et al.[15] reported the formation of hydrogen peroxide by the reaction of the Criegee intermediate with water, though the quoted yield was very different (9% and 0.1%, respectively for isoprene). Simonaitis et al. used flow injection-fluorometric detection of peroxides. Becker et al. utilized diode laser technique and monitored purely gas-phase H_2O_2. The difference can be explained at least to some extent if the intermediacy of HMHP is taken into account. We found HMHP is rather stable in the gas phase, but it decomposes to hydrogen peroxide and formaldehyde in aqueous solution as pointed out by Marklund.[11] However, the yield reported by Simonaitis et al.[14] for isoprene is still higher than ours. The main reason for the difference is still unclear. More investigations are clearly needed.

This study was performed based on the Global Environment Research Program Budget of Environment Agency and partially supported by Grant-in-Aid for Scientific Research (C) (02640462) from the Ministry of Education, Science and Culture.

References

1) D. Möller, *Atmos. Environ.*, 23, 1625 (1989).
2) A.A.F. Kettrup, H.G. Kicinski, and G. Masuch, *Anal. Chem.*, 63, 1047 A (1991).
3) E. Hellpointner and S. Gäb, *Nature (London)*, 337, 631 (1989).
4) C.N. Hewitt and G.L. Kok, *J. Atmos. Chem.*, 12, 181 (1991).
5) C.N. Hewitt, G.L. Kok, and R. Fall, *Nature (London)*, 344, 56 (1990).
6) N. Hewitt and G. Terry, *Environ. Sci. Technol.*, 26, 1891 (1992).
7) K. Izumi, M. Mizuochi, M. Yoshioka, K. Murano, and T. Fukuyama, *Environ. Sci. Technol.*, 18, 116 (1984).
8) S. Hatakeyama and H. Akimoto, *Bull. Chem. Soc. Jpn.*, 63, 2701 (1990).
9) W. Cofer, V. Collins, and R. Talbot, *Environ. Sci. Technol.*, 19, 557 (1985).
10) G.L. Vaghjiani and A.R. Ravishankara, *J. Phys. Chem.*, 93, 1948 (1989).
11) S. Marklund, *Acta Chem. Scand.*, 25, 3517 (1971).
12) S. Hatakeyama, H. Bandow, M. Okuda, and H. Akimoto, *J. Phys. Chem.*, 85, 2249 (1981).
13) H. Niki, P.D. Maker, C.M. Savage, L.P. Breitenbach, and M.D. Hurley, *J. Phys. Chem.*, 91, 941 (1987).
14) R. Simonaitis, K.J. Olszyna, and J.F. Meagher, *Geophys. Res. Lett.*, 18, 9 (1991).
15) K.H. Becker, J. Bechara, and K.J. Brockmann, *Atmos. Environ.*, 27A, 57 (1993).

(Received April 21, 1993)