Formation Mechanism of Peroxides in Reactions of Cyclic Olefins with Ozone in Air

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We carried out reactions of methyl-substituted cyclohexenes and α-pinene with ozone in air and elucidated the mechanisms of formation of the minor products (peroxides and formic acid). Peroxyacetic acid was formed only from the cyclohexenes with a methyl group on the double bond, whereas formic acid was produced in higher yields from the cyclohexenes without a methyl group on the double bond. These differences in product yields allowed us to elucidate the mechanism of formation of the products.

It is currently believed that anthropogenic and/or secondary atmospheric pollutants are closely related to forest decline.[1] Organic hydroperoxides are among the most important of these pollutants. Isoprene and various monoterpenes are emitted into the atmosphere by forest trees,[2,3] and these natural olefins rapidly react with ozone,[4] forming organic hydroperoxides as products.[5]

Previously, we studied reactions of ozone with C_5–C_7 cycloolefins and found that many kinds of C_n and C_{n-1} particulate products are formed in addition to gaseous products.[6] However, in that study, we ignored the minor products formed during the reactions. Nevertheless, these minor products are worth studying, since they are important from the environmental viewpoint.

Here, we have studied the reactions of ozone with various cyclic olefins having a methyl group on the ring and measured the yields of the minor products, i.e., gaseous peroxides (as for general mechanisms and major products of ozone–olefin reactions. See references[7,8]). The position of the methyl group dramatically influenced the yields of the products, which were used to elucidate the reaction mechanisms.

The studied alkenes—α-pinene, 1-methylcyclohexene, 3-methylcyclohexene, and 4-methylcyclohexene (Wako)—were degassed by repeated freeze–thaw cycles before use.

A 6-m^3 photochemical reaction chamber[9] was employed to conduct experiments in the ppmv range. After the chamber was filled with purified air to a pressure of 105 kPa, ozone was introduced into the chamber (1–2 ppmv). The concentration of ozone was monitored with a chemiluminescence ozone analyzer. Then, one of the reactant alkenes was measured volumetrically and introduced into the chamber (2–5 ppmv) with a stream of pure nitrogen. The concentrations of alkene and formic acid product were measured by FTIR spectroscopy.

The concentrations of hydrogen peroxide, methyl hydroperoxide (MHP), hydroxymethyl hydroperoxide (HOCH$_2$OOH, HMHP), and peroxyacetic acid (PAA) were measured with an HPLC−fluorescence detector system after sampling with a mist chamber as reported previously.[5] 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 (bis(hydroxymethyl) peroxide, HOCH$_2$OOCH$_2$OH). BHMP was prepared by Marklund's method.[11] It decomposed to HMHP and H$_2$O$_2$ gradually as reported by Marklund[11] in dilute phosphoric acid at pH 3.5.
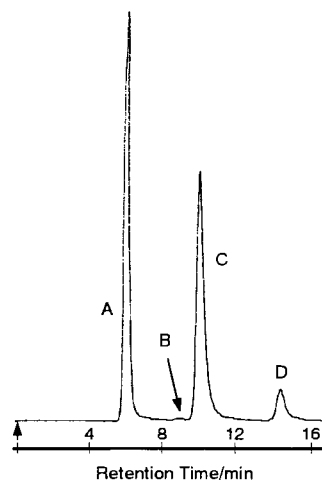

Figure 1. Chromatogram of peroxide products from the reaction of ozone with 1-methylcyclohexene. A, H$_2$O$_2$; B, HMHP; C, MHP; D, PAA.

The chromatogram in Figure 1 shows the peroxide products formed during the reaction of ozone with 1-methylcyclohexene. The yields of the products are listed in Table 1. In Table 1, the yields of formic acid, MHP, and PAA for the upper set of reactants (1-methylcyclohexene and α-pinene) are in clear contrast with those for the lower set of reactants (3-methylcyclohexene and 4-methylcyclohexene).

Scheme 1 shows the initial Criegee cleavage at the double bond of 1-methylcyclohexene as well as 3-methylcyclohexene
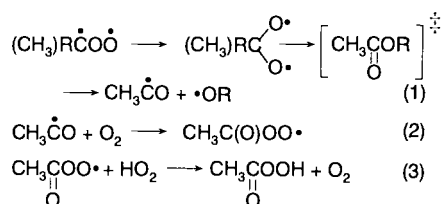
Scheme 1.
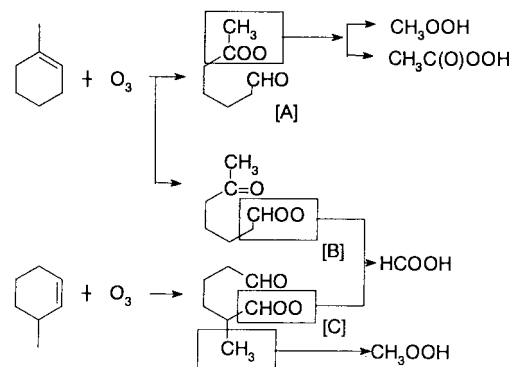
Table 1. Yields of peroxides and formic acid from reactions of ozone with methyl-substituted cyclohexenes and α-pinene
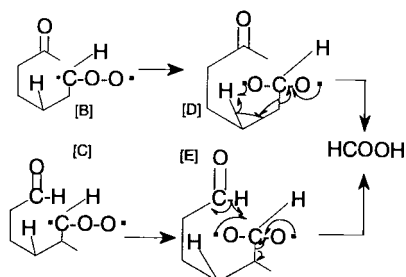
Hydrocarbon	No. of runs	$[HC]_0$/ ppm	$[O_3]_0$/ ppm	H_2O_2	MHP	HMHP	PAA	HCOOH
				Yield / %				
1-Methyl- cyclohexene	3	4.7–4.9	2.0–2.4	0.87	1.06	5.0E–03	0.19	5.6
				0.73	0.95	9.0E–03	0.19	6.0
α-Pinene	3	1.3–1.8	0.9–1.2	0.71	0.65	7.3E–02	0.33	15
				0.74	0.71	8.9E–02	0.39	15
3-Methyl- cyclohexene	4	4.7–4.8	1.7–2.4	0.50	0.03	1.3E–02	0	34
				0.43	0.03	7.0E–03	0	35
4-Methyl- cyclohexene	4	4.7–4.9	2.1–2.3	0.65	0.04	1.3E–02	0	19
				0.57	0.04	1.4E–02	0	20

and subsequent formation of peroxides and formic acid from the substituted Criegee intermediates (RR′COO-type biradical). On the basis of the difference in the structures of the intermediates, we can assume that the fully substituted Criegee intermediate [A] can form PAA. The Criegee intermediate with an H atom can form formic acid. Using the reaction of ozone with 2-methyl-2-butene as a model (in which the ratio of the yield of $(CH_3)_2COO$ to the yield of CH_3CHOO is 7:3 [12]), we can easily rationalize the low yield of formic acid in the reaction of ozone with 1-methylcyclohexene.

The yields of PAA are very interesting. It is clear from Table 1 that a methyl group at the 3- or 4-position of cyclohexene does not promote PAA formation. This suggests that only the Criegee intermediate that has a methyl group at the radical carbon can form PAA. As pointed out by Niki et al.[13] and Martinez and Herron,[14] a doubly substituted Criegee intermediate can isomerize to reactive acetyl esters, and subsequent reactions can take place as follows:

$$(CH_3)\overset{\bullet}{R}C\overset{\bullet}{O}O \longrightarrow (CH_3)RC\overset{O\bullet}{\underset{O\bullet}{\diagup}} \longrightarrow \left[CH_3\underset{O}{\overset{\|}{C}}OR \right]^{\ddagger}$$

$$\longrightarrow CH_3\overset{\bullet}{C}O + \bullet OR \quad (1)$$

$$CH_3\overset{\bullet}{C}O + O_2 \longrightarrow CH_3C(O)OO\bullet \quad (2)$$

$$CH_3\underset{O}{\overset{\|}{C}}OO\bullet + HO_2 \longrightarrow CH_3\underset{O}{\overset{\|}{C}}OOH + O_2 \quad (3)$$

A possible reaction mechanism for the production of formic acid is illustrated in Scheme 2. Since 3- and 4- methyl-

cyclohexenes gave high yields of formic acid, we can assume that only a hydrogen-substituted Criegee intermediate ([B] or [C] in Scheme 1) should be able to produce formic acid. Thus, after transformation of [B] or [C] to a methylenedioxy-type biradical [D] or [E], respectively, formic acid can be formed via one-electron transfers as shown in Scheme 2.

Scheme 2.

References and Notes
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