Reactions of Ozone with 1-Methylcyclohexene and Methylenecyclohexane in Air

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Synopsis. Reactions of ozone with 1-methylcyclohexene and methylenecyclohexane were studied for the purpose of obtaining the reaction mechanism as a prototype of the reaction of ozone with pinenes. The similarity of the yields of corresponding gaseous products between 1-methylcyclohexene and α-pinene and between methylenecyclohexane and β-pinene indicates the similarity of the reaction mechanisms.

Cycloolefins are recognized as precursors of organic aerosols in photochemical smog.[1,2] Previously we reported the study on the mechanism for the ozone–cycloolefin reactions.[3,4] In addition to simple cycloolefins, methylcyclohexenes (1-methyl-, 3-methyl-, and 4-methylcyclohexene) have been reported to exist in gasolines and in ambient air.[5] Thus, the mechanism for the oxidation of such branched cyclic olefins is important from a view point of photochemical aerosol formation.

The oxidation of cycloolefins is also important as a prototype of the atmospheric oxidation of monoterpens. That reaction is paid much attention to since it is assessed to be the most important source of organic aerosols in the troposphere[6,7] as well as one of the largest sources of CO into the atmosphere.[8–10] Recently, we reported the ozone reactions of α- and β-pinene[11] and estimated the gross annual production of CO from natural hydrocarbons by ozone reactions. In order to get an insight into the mechanism for ozone–pinene reactions, 1-methylcyclohexene (**A**) and methylenecyclohexane (**B**), which may be recognized as a prototype of α- (**C**) and β-pinene (**D**), respectively, were studied in this work. To our knowledge no study on the mechanism for those reactions was reported previously.

Experimental

Experimental procedures and analytical techniques are similar to those used in the previous works.[3,4]

Analyses of gaseous products were mainly carried out in the evacuable and bakable photochemical reaction chamber (~6 m^3) by means of FT-IR spectroscopy (~1 ppm of **A** or **B** and ~1 ppm and ~2.6 ppm of ozone for **A** and **B**, respectively). All the experiments were done at 30 °C in 1 atm of air.

For ozone-**B** reaction one run employing $^{18}O_2$ was carried out in a quartz vessel (11 L) equipped with multi-reflection mirrors for FT-IR analysis. The initial conditions were 10 ppm of **B** and 20 ppm of ozone in the presence of 10 Torr (1 Torr=133.322 Pa) of $^{18}O_2$ in pure N_2 at 1 atm.

Gas chromatographic (GC) analysis of gaseous products was also performed by use of 4-L bulbs as reactors at room temperature in 1 atm of air. Initial concentrations of reactions were 70 ppm of cycloolefins and 100 ppm of ozone.

Particulate products were analyzed by means of GC/FID after dissolving the deposited aerosol mist in ether and treating the solution with diazomethane for esterification of acids. Initial concentrations of cycloolefins were 70 ppm and the concentration of ozone was 100 ppm in 4-L bulbs.

1-Methylcyclohexene and methylenecyclohexane were commercially available from Wako. 5-Oxohexanoic acid, 6-oxoheptanoic acid, 2-hexanone, and glutaric acid were obtained from Tokyo Kasei. $^{18}O_2$ of 99% atomic purity was purchased from Nippon Sanso. Ozone was prepared by use of a silent-discharge ozone generator with research grade O_2.

Results and Discussion

Gaseous Products. Gaseous products from the ozone reaction of **A** and **B** analyzed by means of FT-IR were listed in Table 1. The yields of gaseous products from the reactions of ozone with **C** and **D**[11] are also listed for comparison. The main products from **A** were CO, CO_2, formaldehyde, and other aldehydes notified as "Formyls", which would consists of aldehydes, dialdehydes, and keto aldehydes such as glutaraldehyde, 6-oxoheptanal, etc.. Here the yield of "Formyls" was calculated by use of an averaged IR absorption coefficient for the band at 2715 cm^{-1} (0.28 $Torr^{-1}m^{-1}$).[3] In addition to above products 2-hexanone was identified by GC and GC/MS analysis with a molar yield of 3.3±0.3%. CO_2, formaldehyde, and cyclohexanone are the main products from **B**. Formic acid from both reactants and CO from **B** seemed secondary products since their yield increases with reaction time.

Figures 1 and 2 show typical time profiles of the reactants and products in ozone–**A** and ozone–**B** reactions, respectively. In contrast to the constancy of other gaseous products, the decay of "Formyls" in Fig. 1 after reaching a maximum was observed. It should

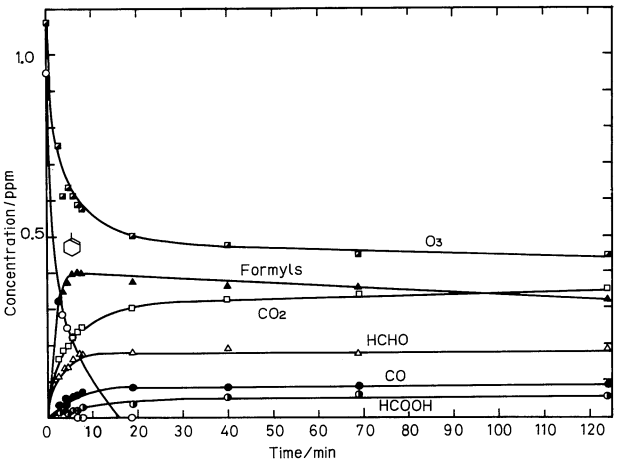

Fig. 1. Typical time profiles of the concentrations of reactants and products in 1-methylcyclohexene (1 ppm)–ozone (1 ppm) reaction.

Table 1. Initial Conditions, Stoichiometry, and Product Yields for Ozone Reactions with 1-Methylcyclohexene, α-Pinene, Methylenecyclohexane, and β-Pinene

Reactant olefin	$[Olefin]_0$ / ppm	$[Ozone]_0$ / ppm	$\Delta[Olefin]/\Delta[Ozone]$
1-Methylcyclohexene (**A**)	~1.0	~1.2	1.62
α-Pinene (**B**)	~0.8	0.6—1.4	1.48
Methylenecyclohexane (**C**)	~1.0	~2.5	1.55
β-Pinene (**D**)	~0.8	1.3—2.5	1.18

Reactant olefin	Molar yield of products/%[a]					
	CO	CO_2	HCHO	HCOOH	Formyls or ketone	Reference
1-Methylcyclohexene (**A**)	6.9	26.4	18.5	0— 3[b]	60	This work
α-Pinene (**B**)	8.7	29.8	21.9	0—10[b]	51	Ref. 11
Methylenecyclohexane (**C**)	0—10[b]	31.4	82.9	0— 5[b]	55.3[c]	This work
β-Pinene (**D**)	0— 8[b]	26.6	76.1	<1	40.0[d]	Ref. 11

a) The yield averaged for five runs. b) 0—x means that the yield increased from 0 to x% in the course of the reaction. c) Cyclohexanone. d) 6,6-Dimethylbicyclo[3.1.1]heptan-2-one.

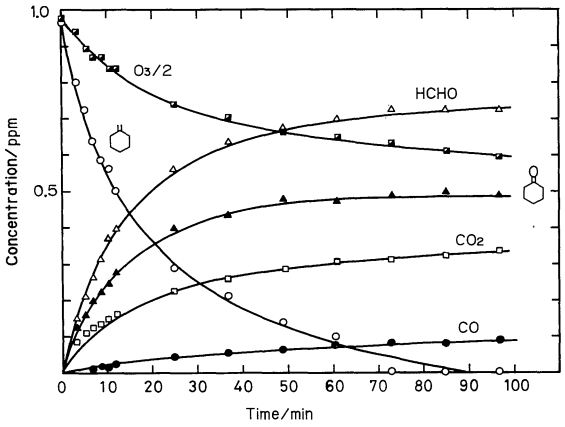

Fig. 2. Typical time profiles of the concentrations of reactants and products in methylenecyclohexane (1 ppm)–ozone (2 ppm) reaction.

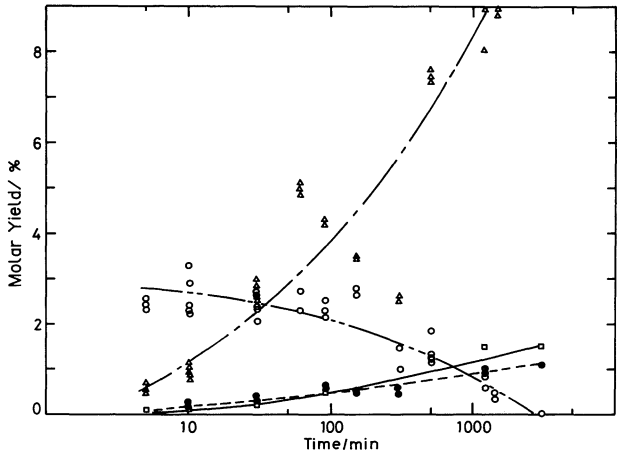

Fig. 3. Time profiles of the yields of particulate products form 1-methylcyclohexene (70 ppm)–ozone (90 ppm) reactions. ○: 6-oxoheptanal, △: 6-oxoheptanoic acid, □: glutaric acid, ●: 5-oxohexanoic acid.

be due to the gas-to-particle conversion and deposition on the wall.

The similarity of the yields of gaseous products between **A** and **C** and between **B** and **D** is clear from Table 1. It strongly suggests that the reactions of ozone with **C** and **D** proceed similarly to those with **A** and **B**, respectively.

Particulate Products. Particulate products identified were 5-oxohexanoic acid [$CH_3CO(CH_2)_3COOH$], 6-oxoheptanoic acid [$CH_3CO(CH_2)_4COOH$], glutaric acid [$HOOC(CH_2)_3COOH$], and 6-oxoheptanal [$CH_3CO(CH_2)_4CHO$] from ozone–**A** reactions. No product other than cyclohexanone was identified from ozone–**B** reactions in the extracted ether solution except for an unidentified chromatographic peak. Figure 3 shows the time profile of the yield of each particulate product from ozone–**A** reactions. As in the case of the ozone–unsubstituted cycloolefin reactions,[3,4] aldehyde (only 6-oxoheptanal was identified) decreased, and acids increased monotonously with time. It is in accord with the contention that the sequential oxidation of aldehyde to acid occurs probably on the reactor wall or on the surface of aerosols.

Reaction Mechanism. Figure 4 shows the reaction scheme for the ozone–**A** reaction. Path I gives a singly substituted Criegee intermediate. It is similar to those produced in ozone-unsubstituted cycloolefin reactions, so that similar products can be anticipated. In fact 2-hexanone, 5-oxohexanoic acid, and 6-oxoheptanoic acid were observed. These compounds correspond to pentanal, glutaric acid, and adipic acid, respectively, from the ozone–cyclohexene reaction.[3] Path II gives a doubly substituted Criegee intermediate. Recently, Niki et al.[12] and Martinez and Herron[13] reported that the doubly substituted Criegee intermediate such as $(CH_3)_2\dot{C}OO\cdot$ reacted differently compared with the unsubstituted or the singly substituted ones. Intramolecular hydrogen migration to form a hydroperoxyalkene and its subsequent decomposition were postu-

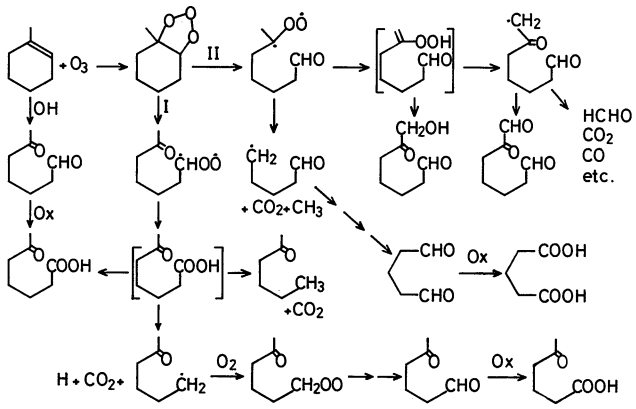

Fig. 4. Reaction mechanism for 1-methylcyclohexene–ozone reaction.

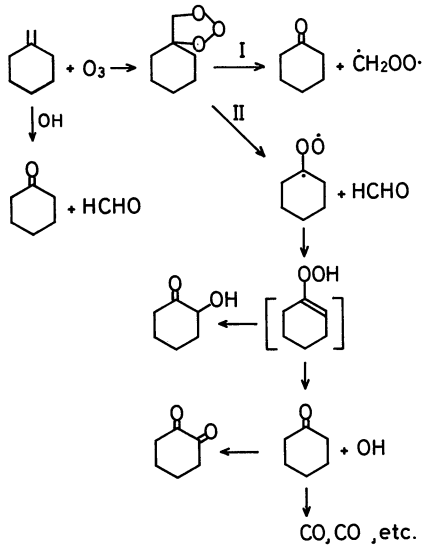

Fig. 5. Reaction mechanism for methylenecyclohexane–ozone reaction.

lated to explain the formation of hydroxyacetone (CH_3COCH_2OH) and methylglyoxal (CH_3COCHO). No products corresponding to those compounds were positively identified in this work. However, similar compounds were reported as products of the ozone–**C** reaction by Hull.[14] Production of glutaric acid observed in this study suggests a similar decomposition through Path II.

As depicted in Table 1, the ratio of the decreased amount of **A** to that of ozone was always larger than unity. By analogy with our previous conclusion[3,4] this should also be due to the reaction of OH radicals. In fact the formation of 6-oxoheptanal is difficult to explain without the reaction of OH with **A** (as for the detailed mechanism, see Refs. 3 and 11). In the ozone–**B** reaction in N_2 (1 atm) in the presence of $^{18}O_2$ (10 Torr), ^{18}O-labelled cyclohexanone was observed. It clearly shows the participation of hydroxyl (^{18}OH) radicals.

Figure 5 shows the conceivable reaction paths for ozone–**B** reactions. Path I is to give cyclohexanone and an unsubstituted Criegee intermediate. Subsequent reactions of the intermediate are now well-established.[15,16] Path II is the formation of formaldehyde and a doubly substituted Criegee intermediate. Subsequent reactions of this intermediate should be as described above. Neither hydroxy ketone-type compounds nor cyclic diketone-type compounds were identified, whereas such kinds of products were observed by Hull[14] from ozone–**D** reactions.

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