



# Gas-Phase Production and Loss of Isoprene Epoxydiols



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## 1. Introduction

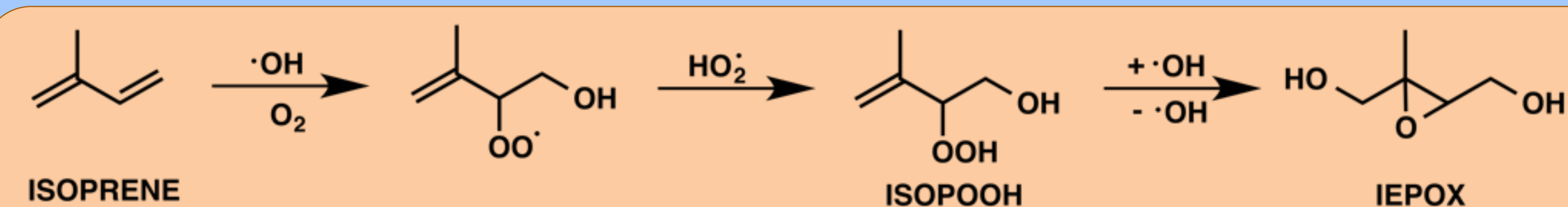


Figure 1. Steps in the formation of IEPOX from isoprene by atmospheric oxidation.

### What is an isoprene epoxydiol (IEPOX)?

→ IEPOX is a second-generation oxidation product of isoprene, formed by the gas-phase reaction of isoprene with OH in low-NO environments (as shown in Figure 1).<sup>1</sup>

→ Four possible isomers of IEPOX can be formed by isoprene (Figure 2).

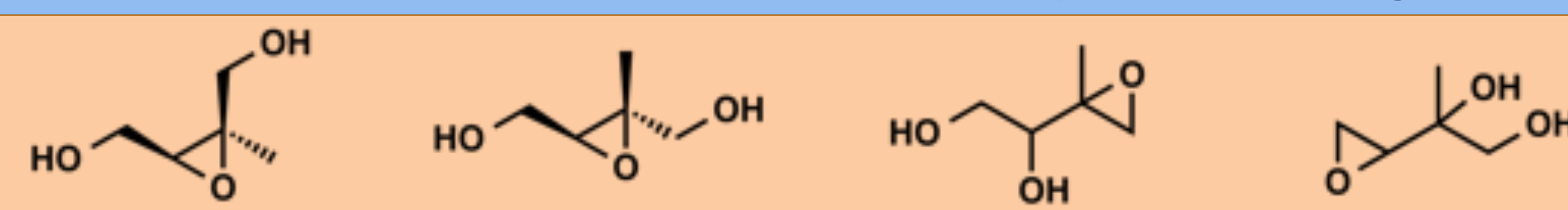


Figure 2. The four isomers of IEPOX.

### Why is IEPOX important?

→ Isoprene oxidation estimates show that 95 ± 45 TgC/y of IEPOX forms globally.<sup>1</sup>

→ The oxidation mechanism leading to IEPOX regenerates one equivalent of OH, partially accounting for the stability of HO<sub>x</sub> levels observed in remote forest regions.<sup>1-4</sup>

→ IEPOX contributes to secondary organic aerosol (SOA) formation, as its low volatility and high water solubility allow it to partition into the condensed phase. Uptake of IEPOX onto acidic aerosol has been shown to contribute significantly to SOA in forested areas where anthropogenic pollutants (e.g. SO<sub>2</sub>) are present.<sup>5-9</sup>

### Here, we report:

- A. The rate constants for gas phase oxidation of IEPOX by OH (relative to propene).
- B. The relative amounts of IEPOX isomers formed by *in situ* oxidation of isoprene.
- C. The products of gas phase oxidation of IEPOX by OH.

## 2. Methods

### Synthesis:

δ1-, and cis-β-, and trans-β-IEPOX were synthesized according to procedures described by Zhang et al. and Hoang et al. with minor adjustments; synthetic schemes are shown in Figure 3.<sup>10-11</sup>

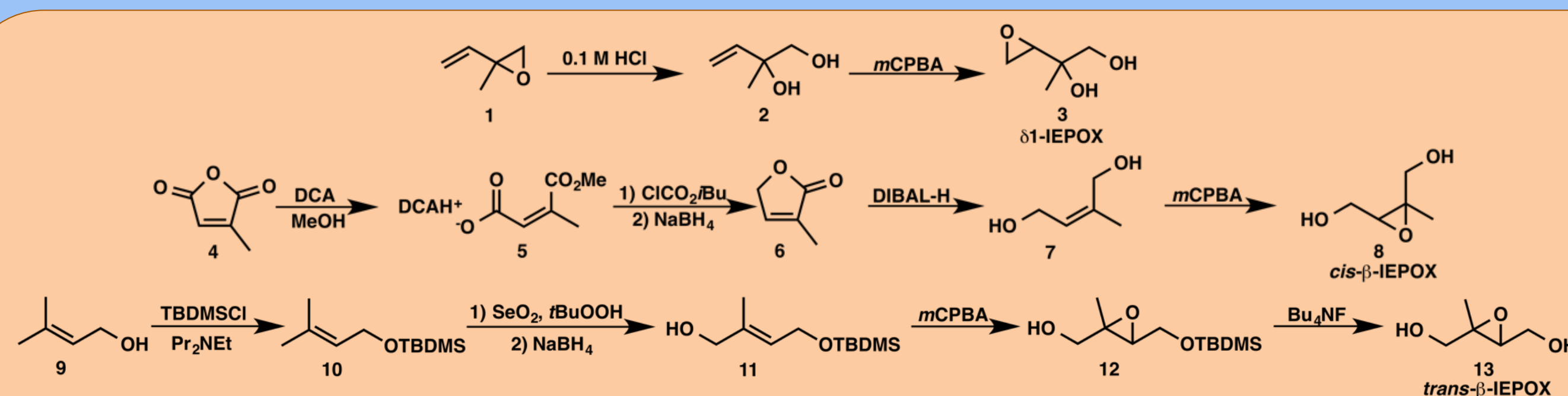


Figure 3. Schemes for the synthesis of δ1-, cis-β-, and trans-β-IEPOX.

### Oxidation experiments:

Gas-phase oxidation experiments were performed in a 0.85 m<sup>3</sup> fluorinated ethylene propylene copolymer (Teflon-FEP, Dupont) chamber at 1 atm. Hydrogen peroxide provided the source of HO<sub>x</sub> for oxidation upon photolysis under UV lights. Along with H<sub>2</sub>O<sub>2</sub> (2.5 ppm ± 10%), IEPOX (30 ppb ± 50%), NO (0 or 500 ppb), and propene (0 or 100 ppb) were injected into the chamber before photooxidation. Photooxidation lasted 3-7 h. Nine gas-phase photooxidation experiments were performed, along with two experiments without oxidation to monitor loss of IEPOX to surfaces. The chamber's contents were monitored by time-of-flight CF<sub>3</sub>O<sup>-</sup> chemical ionization mass spectrometry (ToF-CIMS, Tofwerk/Caltech), triple quadrupole MS-MS CF<sub>3</sub>O<sup>-</sup> CIMS (Varian/Caltech), gas chromatography with flame-ionization detection (GC-FID Agilent 5890 II), NO<sub>x</sub> Monitor (Teledyne 200EU), and O<sub>3</sub> monitor (Teledyne 400E). Before and after photooxidation, monitoring was interrupted to sample compounds by gas chromatography before detection by ToF-CIMS (GC-CIMS), which allowed for separation of IEPOX isomers.

## 3. Results: IEPOX + OH Rate

Six experiments were performed to measure IEPOX + OH rate coefficients: one for each isomer at high- and low-NO conditions. Rate coefficients were calculated relative to that of OH + propene (2.62 × 10<sup>-12</sup> cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> at 299 K)<sup>12</sup>, which was injected into the chamber along with IEPOX.

Calculated OH oxidation rate coefficients and lifetimes for the three IEPOX isomers at 299 K and [OH] = 10<sup>6</sup> molec cm<sup>-3</sup> are shown in Table 1.

	δ1-IEPOX	cis-β-IEPOX	trans-β-IEPOX
k × 10 <sup>11</sup> (std dev) cm <sup>3</sup> molec <sup>-1</sup> s <sup>-1</sup>	0.84 (±0.07)	1.52 (±0.07)	0.98 (±0.05)
Lifetime (std dev) hours	33.0 (±2.8)	18.3 (±0.8)	28.3 (±1.4)

Table 1. IEPOX + OH rate coefficients and lifetimes.

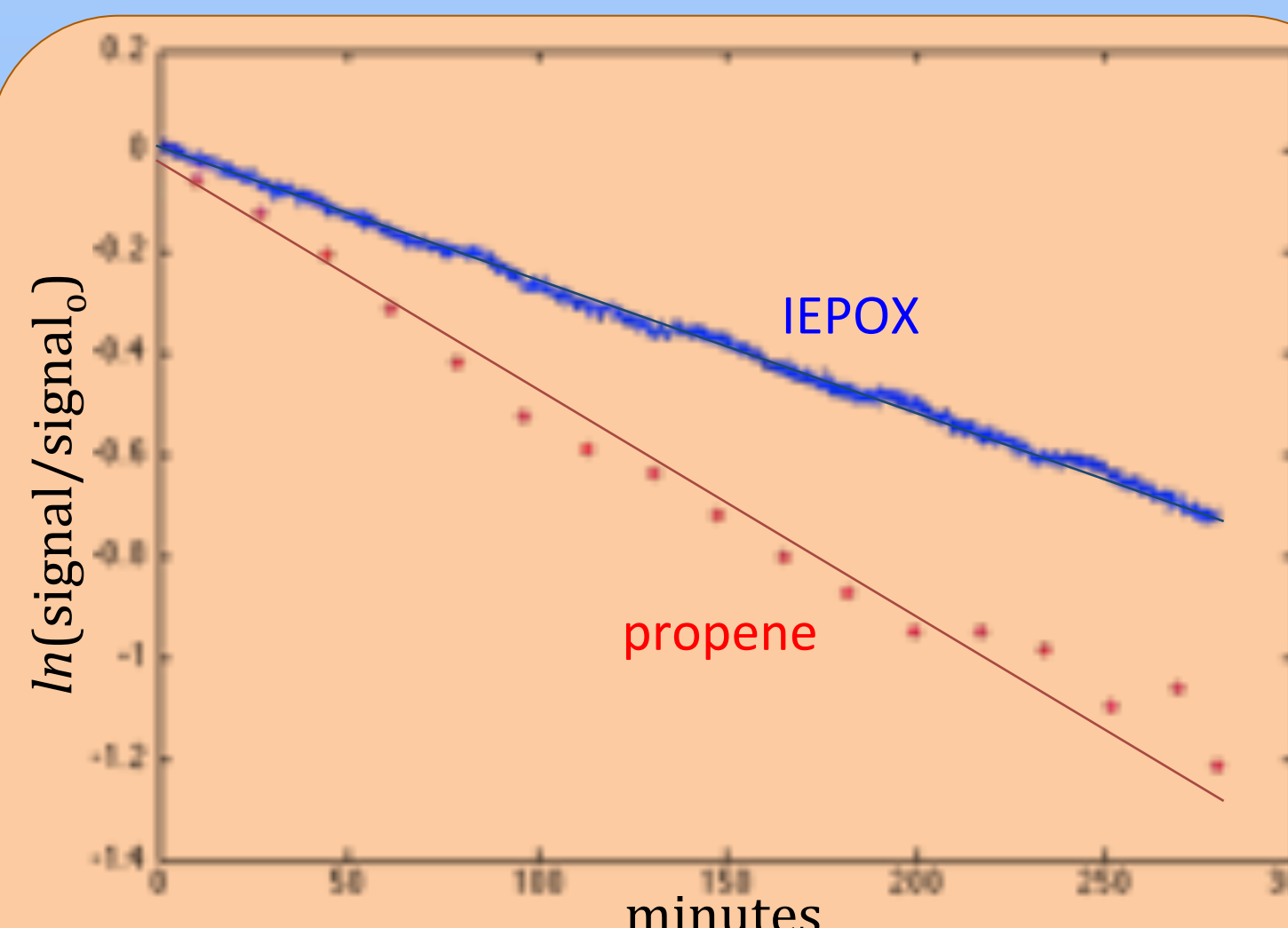


Figure 4. Decay of cis-β-IEPOX and propene over the course of photooxidation.

Rate coefficients were calculated using a linear regression method incorporating error in both dimensions, followed by an error-weighted mean of each isomer's high- and low-NO experiments.

## 4. Results: Isomer Yield

Isoprene was oxidized by OH in a low-NO chamber experiment, similar to those carried out on IEPOX; GC-CIMS detection of oxidation products (Figure 5) was performed after 1 h and 10 h of oxidation.

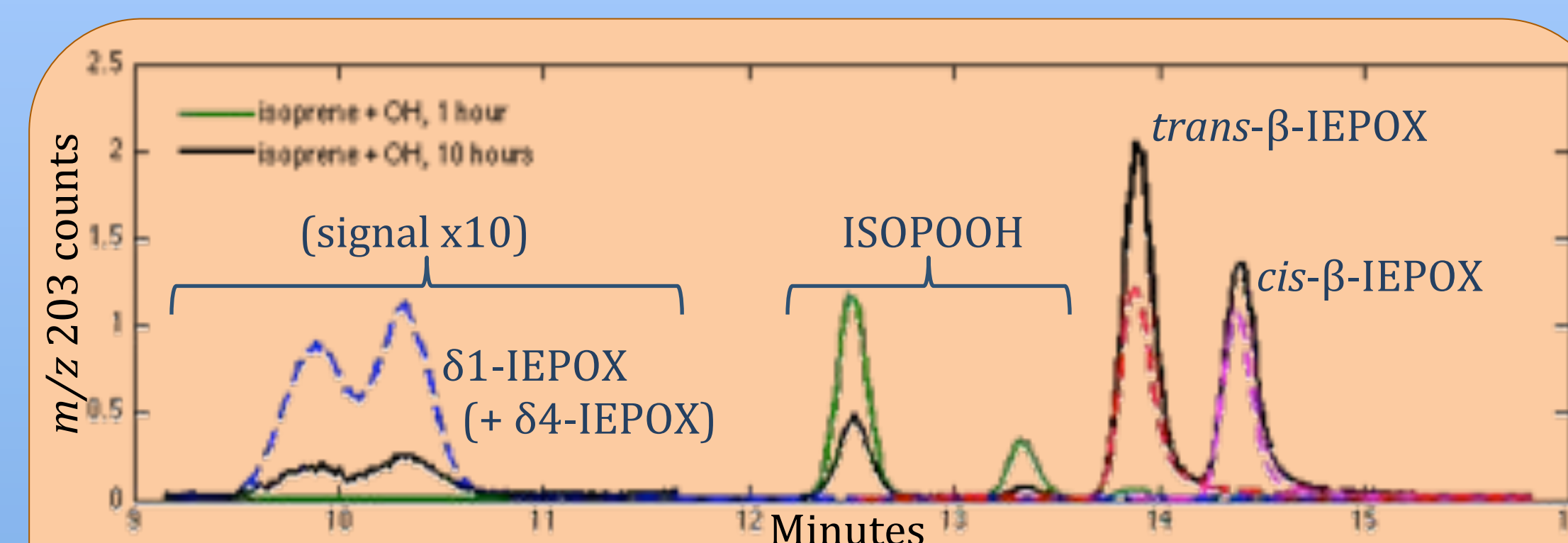


Figure 5. GC-CIMS trace from synthesized IEPOX standards (dashed lines) and m/z 203 products of low-NO isoprene photooxidation.

From the differences in peak areas after 10 h of isoprene oxidation by OH, along with differences in CIMS sensitivity and OH oxidation rates between the IEPOX isomers, we find that OH-initiated low-NO oxidation of isoprene produces 31 ± 5 % cis-β and 66 ± 4 % trans-β-IEPOX. δ1- and δ4-IEPOX together account for <3% of IEPOX produced. The ratio of cis- and trans- yields is similar to (and may explain) the ratio of 2-methyltetrol isomers found in SOA created by oxidation of isoprene by OH.<sup>9, 13-16</sup>

## 6. Atmospheric Implications

### The results presented here:

- Reduce the uncertainty in the rate of gas-phase IEPOX loss, which aids in estimation of IEPOX concentrations, SOA formation, and product formation.
- Show that only two of the four proposed IEPOX isomers form under typical atmospheric conditions, narrowing the necessary scope of further investigation.
- Help explain the ratio of 2-methyltetrol isomers found in isoprene-derived SOA, and may close some of the disagreement between modeled and observed concentrations of glyoxal and methylglyoxal, two proposed products of IEPOX oxidation.
- Will improve modeling of low-NO isoprene oxidation by constraining gas-phase IEPOX oxidation products and providing a tentative mechanism for IEPOX oxidation.

## 5. Results: Product Studies

Isomer:	cis-β	cis-β	trans-β
Products:	high NO	low NO	high NO
C <sub>5</sub> O <sub>3</sub> H <sub>8</sub> *	10.6 ± 0.7	12.9 ± 1.0	10.5 ± 0.3
C <sub>4</sub> O <sub>3</sub> H <sub>8</sub> *	46.4 ± 1.7	37.1 ± 2.2	21.7 ± 0.5
C <sub>4</sub> O <sub>3</sub> H <sub>6</sub> *	14.4 ± 0.6	10.4 ± 0.6	3.7 ± 0.2
glycolaldehyde	12.6 ± 0.5	3.0 ± 0.7	4.9 ± 0.3
hydroxyacetone	16.0 ± 0.3	8.1 ± 0.5	5.1 ± 0.2
acetic acid	4.0 ± 0.3	7.2 ± 1.1	2.4 ± 0.3
formic acid	10.4 ± 0.3	18.3 ± 1.4	5.8 ± 0.3

Table 2. First-generation yields (%) of dominant products from oxidation of cis- and trans-β-IEPOX by OH. (\*see proposed structures in Fig. 7)

Oxidation experiments performed in the absence of propene were used to determine the products of gas-phase OH oxidation of cis- and trans-β-IEPOX. Products were detected by ToF-CIMS and MS-MS CIMS, and signals were scaled by a sensitivity calibration factor. First-generation yields were calculated by determining the slope of a linear regression between the mixing ratios of IEPOX and each product over the first 10-20 minutes of oxidation.

Time traces of oxidation products are shown in Figure 6, and yields of major first-generation products are shown in Table 2.

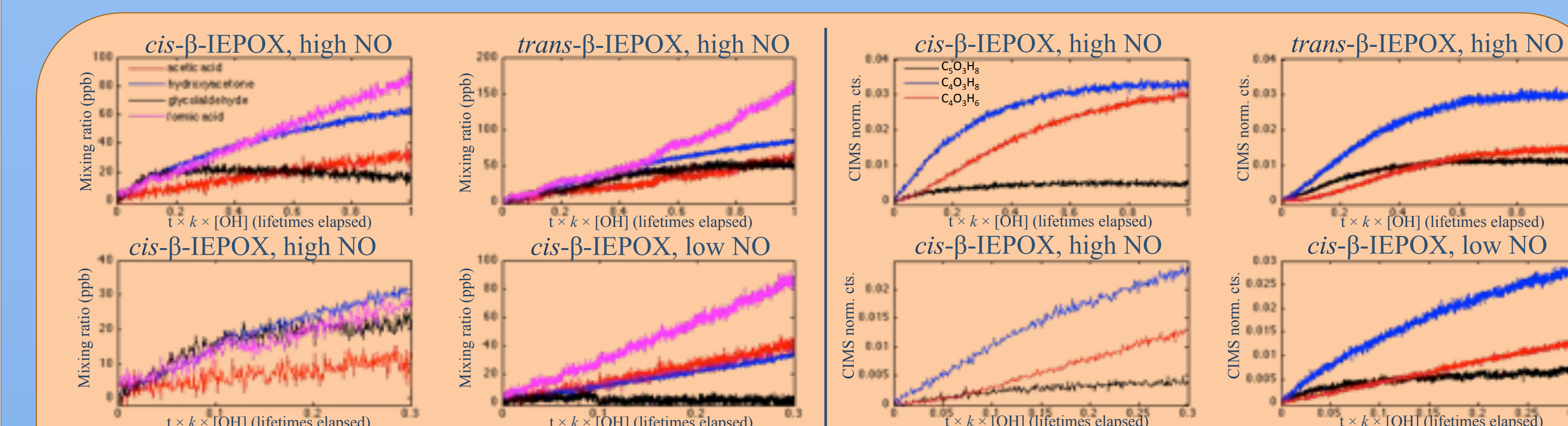


Figure 6. Time traces of dominant small (left panels) and large\* (right panels) first-generation products observed in the oxidation of cis- and trans-β-IEPOX by OH. (\*see structures in Fig 7)

Based on the first-generation products observed, we propose a tentative new mechanism for the OH-initiated oxidation of β-IEPOX (Fig. 7). This mechanism explains the formation of novel C<sub>4</sub>-C<sub>5</sub> products (C<sub>5</sub>O<sub>3</sub>H<sub>8</sub>, C<sub>4</sub>O<sub>3</sub>H<sub>8</sub>, and C<sub>4</sub>O<sub>3</sub>H<sub>6</sub>), and accounts for the low dependence of product yields on NO concentrations, but does not yet explain differences in product yields between the β-IEPOX isomers or the formation of C<sub>1</sub>-C<sub>2</sub> acids.

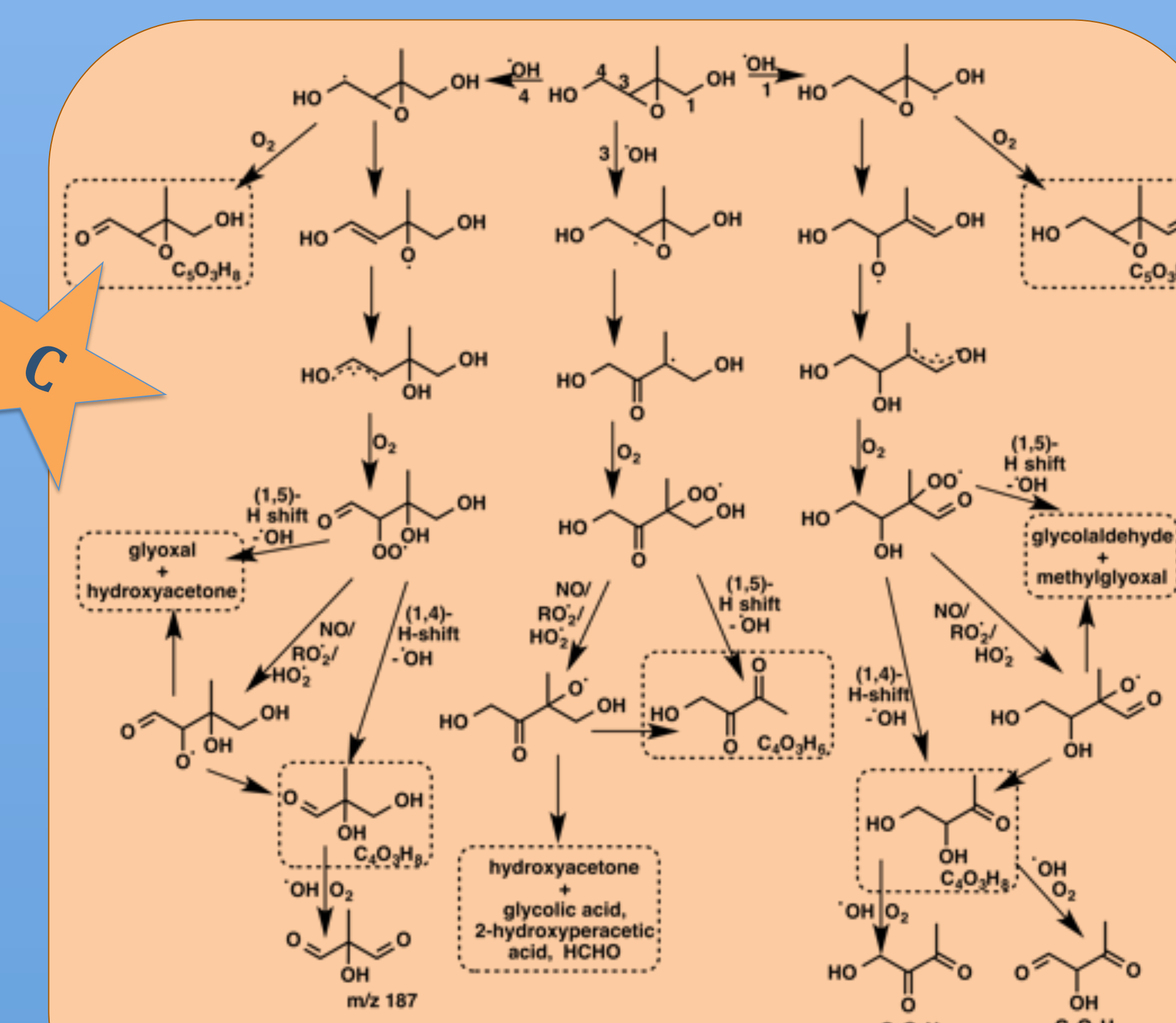


Figure 7. Proposed mechanism of OH-initiated oxidation of β-IEPOX (1<sup>st</sup>-generation products in boxes)

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