Supporting Information

Effect of molecular structure on epoxidation of allylic olefins by atomic O on Au

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^{18}O isotopic labeling for product identification

General experimental method

In the oxygen isotopic labeling experiments, before the exposure to allylic olefins, the surface was covered with a mixture of ^{16}O and ^{18}O by using $H_2{}^{18}O$ as an exchange agent. An ^{16}O-covered surface with the initial coverage of 0.2 monolayer was first prepared by exposure to ozone at 200 K, $H_2{}^{18}O$ was then condensed at 180 K on the surface. The surface then was annealed to 250 K to drive off all the water molecules. Due to the proton exchange between water and adsorbed oxygen, some of the ^{16}O is replaced by ^{18}O. As a result, chemisorbed oxygen on the surface was composed of both ^{16}O and ^{18}O with a typical ratio of 2:1. Therefore, the products obtained from the reactions of olefins with such a surface consisted of both ^{16}O and ^{18}O. By examining the increase in masses of the parent ions/fragment ions, the stoichiometry of the products/fragments could be confirmed. Further, the identity of the products could be revealed.

Identification of phenylvinyl ketone

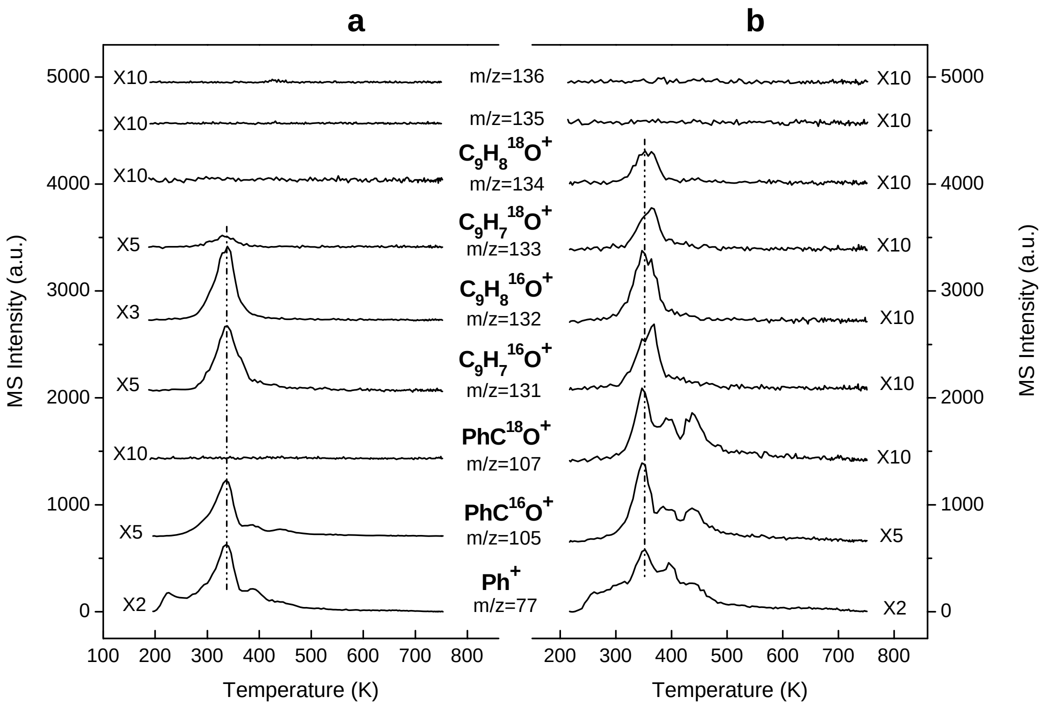

Figure S1 Formation of phenylvinyl ketone in the reaction of allylbenzene with (a) ^{16}O and (b) a mixture of ^{16}O and ^{18}O (^{16}O:^{18}O ~ 2:1). The stoichiometry of this product is provided by the mass shift of +2 for the parent ion (M) and the (M-1) ion in (b). Its identification is confirmed by the +2 mass shift for the fragment m/z 105 and no shift for the fragment m/z 77 in (b).

Isotopic labeling of the oxygen overlayer was used to identify phenylvinyl ketone formed at 330 K in the oxidation of allylbenzene. In the reaction with ^{16}O, this product shows mass fragments with m/z 133, 132, 131, 105 and 77 (Figure S1a); m/z 133 shows a very weak peak and is one mass above the parent ion, primarily due to the natural isotope abundance of ^{13}C. The stoichiometry of this product was determined to be C_9H_8O from the parent ion m/z 132. The peak intensity of m/z 133 is about 10 % of that of m/z 132 (Table S1), consistent with the expected ratio (10.1 %) based on the isotope abundance of ^{13}C (1.1078 %, IUPAC) and the number of carbon atoms in the molecule. Loss of one hydrogen atom results in the fragment m/z 131. The most intense fragment (m/z 77) can be assigned as C_6H_5, and the second most intense fragment (m/z 105) is a signature fragment for molecules consisting of the C_6H_5CO linkage. Its identification is further confirmed in the reaction spectra from the oxygen isotopic labeling (Figure S1b). The relative intensity of each fragment is shown in Table S1. The oxidation of allylbenzene yields products at the same temperature showing parent ions of m/z 132 ($C_9H_8{}^{16}O$) and 134 ($C_9H_8{}^{18}O$). The ratio of these two parent ions is ~ 2:1, consistent with that of pre-adsorbed ^{16}O and ^{18}O. The ion m/z 135 is not detected, probably because its intensity is below the noise level. The mass of the fragment ion C_6H_5CO (m/z 105) shifts by +2, while C_6H_5 does not. As can be readily calculated from Table S1, the ratios of ion $C_6H_5C^{16}O$ to $C_9H_8{}^{16}O$ (2.15) and $C_6H_5C^{18}O$ to $C_9H_8{}^{18}O$ (2.20) in the isotopic labeling experiment, are consistent with that of C_6H_5CO to C_9H_8O (2.26) in the non-isotopic labeling experiment; likewise, the ratio of ion C_6H_5 to the sum of $C_9H_8{}^{16}O$ and $C_9H_8{}^{18}O$ is in reasonable agreement with that of C_6H_5 to C_9H_8O. The consistency in the yields of fragment ions in the two series of reaction spectra further validates the assignment of this product to phenylvinyl ketone.

Table S1 Fragmentation patterns for the product with stoichiometry C_9H_8O in the reaction of allylbenzene with ^{16}O and a mixture of ^{16}O and ^{18}O

oxygen on gold	m/z (relative intensity ± 10%)							
	77	105	107	131	132	133	134	135
^{16}O	271	226	–	64	100	10	–	–
$^{16}O + {}^{18}O$	420	215	99	70	100	44	45	–

Stoichiometry of product with parent ion of m/z 148

The same analytical method was applied to attribute the product with parent ion of m/z 148 to $C_6H_5COC_2H_3O$. Briefly, it exhibits a parent ion (M) with m/z 148, an (M-1) ion with m/z 147 by losing one hydrogen, and two other intense ion fragments of m/z 105 and 77. In the oxygen isotopic labeling experiments, mass shifts of both +2 and +4 were observed for the parent ion (M) as well as the (M-1) ion, corresponding to the incorporation of one and two ^{18}O into this product, respectively. Clearly this product contains two oxygen atoms, as expected for $C_9H_8O_2$. Similar to what was discussed in the identification of phenylvinyl ketone, the 105 ion shifts by mass +2, while there is no shift to the 77 ion, strongly suggesting the presence of a C_6H_5CO linkage. However, the arrangement of atoms in the pendant C_2H_3O remains to be determined. It could be –CH(O)CH_2, or –CH_2CH=O. The formation of benzoylmethyl ketone ($C_6H_5COCOCH_3$), with –$COCH_3$ being the pendant, can be readily excluded because the mass fragmentation pattern provided by NIST is quite different from what we observed.

Quantification of carbon deposit in the oxidation of the three olefins

In addition to the gaseous products liberated, carbonaceous species are deposited on the Au surface after each reaction. As shown in Figure S2, CO_2 and H_2O are formed from combustion of the surface deposit in the post-oxidation experiments. CO_2 peaks evolve at 420-430 K (Figure S2a and c), and H_2O peaks are centered at 410-420 K (Figure S2b and d). It is clearly shown that in all of the post-oxidation reactions, the amount of CO_2 evolved is substantially larger than that of H_2O, showing that the residual species are rich in carbon. This indicates that the surface deposit may be formed by dehydrogenation of the allylic olefins, which can be initiated through the stripping of the allylic hydrogens by chemisorbed oxygen. When the initial oxygen coverage for the oxidation of olefin is higher, more carbonaceous species are deposited on the surface

(Figure S2b and d). It is also noteworthy that the amount of carbonaceous residue is about the same for all three isomers with the same initial oxygen coverage.

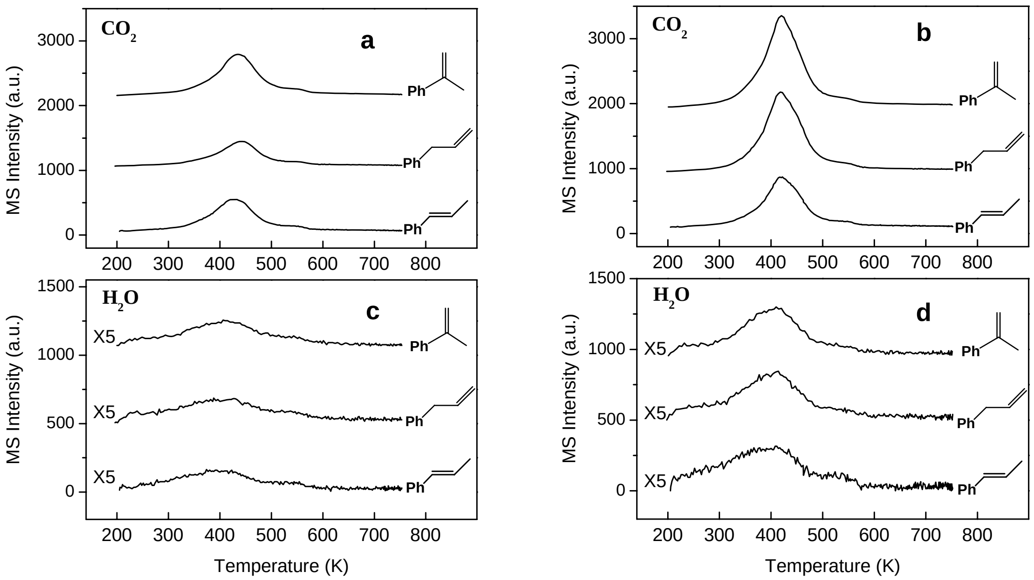

Figure S2 Temperature-programmed reaction after exposure to ozone at 200 K until saturation, subsequent to the reactions of the three allylic olefins with chemisorbed oxygen at two different initial coverages of 0.2 (a, c) and 1 (b, d) monolayer. CO_2 (a, b) and H_2O (c, d) are formed in these post-oxidation reactions.

Table S2 Relative amounts of residual carbonaceous species in the oxidation of *trans*-*β*-methylstyrene, *α*-methylstyrene, and allylbenzene on Au

Olefins	Peak Area of CO_2 in Post-oxidation		Relative Ratio	
	θ_O = 0.2 monolayer	θ_O = 1 monolayer	θ_O = 0.2 monolayer	θ_O = 1 monolayer
trans-*β*-methylstyrene	591568	791753	1.00	1.00
α-methylstyrene	651489	1278119	1.10	1.61
allylbenzene	390159	1141110	0.66	1.44