

## Surface Science Letters

O(<sup>3</sup>P) reactions with small alkenes adsorbed on Rh, Au, and ice

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**Abstract**

Using molecular beams, we studied the reaction of O(<sup>3</sup>P) with 1- and 2-butene on the surface of Rh(111) and ice, and propene on the surface of Au(111), in vacuum at cryogenic temperatures. Unlike in the gas phase, and similar to reactions in the condensed phase, only the oxygen addition products were observed. The surface serves as a sink for the excess energy of this highly exoergic process, stabilizing the adduct product channels.

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**1. Introduction**

The reaction of O(<sup>3</sup>P) with alkenes is a relatively important elementary reaction in understanding combustion chemistry. The formation of epoxides from the addition of oxygen to the double bond is also of technological importance for manufacturing many useful substances. O(<sup>3</sup>P) reactions have been extensively studied both in the gas phase [1–6], under single and multiple collision conditions, and in the condensed phase [7–11]. The activation energy for the insertion of the oxygen is low, at most ~10 kJ/mole, and the exoergicity for the formation of an epoxide or carbonyl is on the order of 400 kJ/mole [1]. The initial step is the attachment of the oxygen to the less substituted carbon of the double bond forming a triplet biradical. This can either directly decompose or undergo an intersystem crossing to the singlet surface and form an epoxide or carbonyl addition compound. Because of the reaction exoergicity, these products are not stable unless there is some way to dispose of the excess energy. For low gas pressures, the products of vapor phase reactions are associated with fragmentation and rearrangement

pathways. In the condensed phase, or at higher gas pressures where there are multiple collisions, the excess energy can be dissipated and the addition products dominate.

Previous studies of the reactions of condensed alkenes with O(<sup>3</sup>P) have involved thick layers, either neat or diluted in propane, or as a solution with liquid nitrogen using several Torr of ambient oxygen atoms [7–9]. In this paper, we will examine the reaction of O(<sup>3</sup>P) with adsorbed 1- and 2-butene on the surfaces of both Rh(111) and amorphous ice and propene adsorbed on Au(111). These experiments were done at cryogenic temperatures and under ultra-high vacuum (UHV) conditions, using molecular beams for exposing the surface to the reactants. At the surface temperatures of our experiments,  $T_s = 115$ – $120$  K for the butenes and ~130 K for the propene, the alkenes are only transiently adsorbed at a submonolayer coverage. Post-reaction temperature-programmed desorption (TPD) was used to detect products that remained adsorbed on the surface. We were also able to search for volatile products formed during the reaction. Only the addition products were observed, which remained on the surface until heated. During reaction between the alkenes and oxygen, the surface channels the excess energy away from the oxygen addition products, which serves to stabilize them.

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## 2. Experimental

The machine has been extensively described elsewhere [12,13], and only the essential features will be covered. There is the provision to make three independent molecular beams which converge in the UHV chamber at the position of the Rh(111) crystal. Molecules scattered from or produced on the surface are detected by a differentially-pumped quadrupole mass spectrometer that can be rotated around the position of the crystal. For most of the experiments, the incident polar angle was  $45^\circ$ , and the detection done between  $0^\circ$  and  $5^\circ$  with respect to the surface normal. For investigating the production of volatile products, the center molecular beam can be mechanically chopped before it reaches the crystal.

We used both 5%  $O_2$  in He and low pressure neat  $O_2$  to produce the O atoms in a quartz-nozzle radio-frequency plasma beam source. The average O atom kinetic energy was 200 meV (19 kJ/mol) for the He seeded beam, and 66 meV (6 kJ/mol) for the neat beam. The flux of O was highest for the seeded beam,  $\sim 0.05$  monolayers/s ( $ML/s \equiv 1.6 \times 10^{15}/cm^2 s$ ). The alkene beam was either neat 1-butene, neat propene, or a mixture of *cis*- and *trans*-2-butene with a comparable flux at the crystal as that of the O atoms. For experiments on the surface of ice, the cold Rh (115–120 K) was exposed to a separate beam of He bubbled through an  $H_2O$ -filled container.

The experimental procedure was to expose the surface to concurrent beams of alkene and  $O(^3P)$ . While this was occurring we could search for volatile reaction products. After exposing the crystal for typically 20 min the reaction products that remained on the surface were measured by TPD, where the surface temperature is ramped while monitoring desorbing molecules with the line-of-sight and differentially-pumped mass spectrometer. Because of the narrow angular resolution of the detector ( $1^\circ$ ), there were relatively low signal levels. A few masses were measured during each exposure via computer-controlled tuning of the mass spectrometer while the temperature of the crystal was ramped. To get all of the masses, consecutive experiments were necessary. For comparison, one of the detected masses was the same for each experiment and its value was used to normalize the results.

For the determination of the reaction products, it was also necessary to determine the precise fragmentation pattern of the proposed possible products. For Rh, we adsorbed the proposed products and the fragmentation pattern was determined by TPD. For Au, the fragmentation pattern was measured by collecting mass spectra of the proposed products scattering from the crystal surface. It is important to note that because of differences in the vapor pressure of the products, and thus the beam flux, and possible differences the adsorption probabilities, the quantitative comparison between different products is imprecise; the relationship between the signal intensity and the amount of product is semi-quantitative. An idea of the statistical error is shown in Fig. 1a, where the results for the

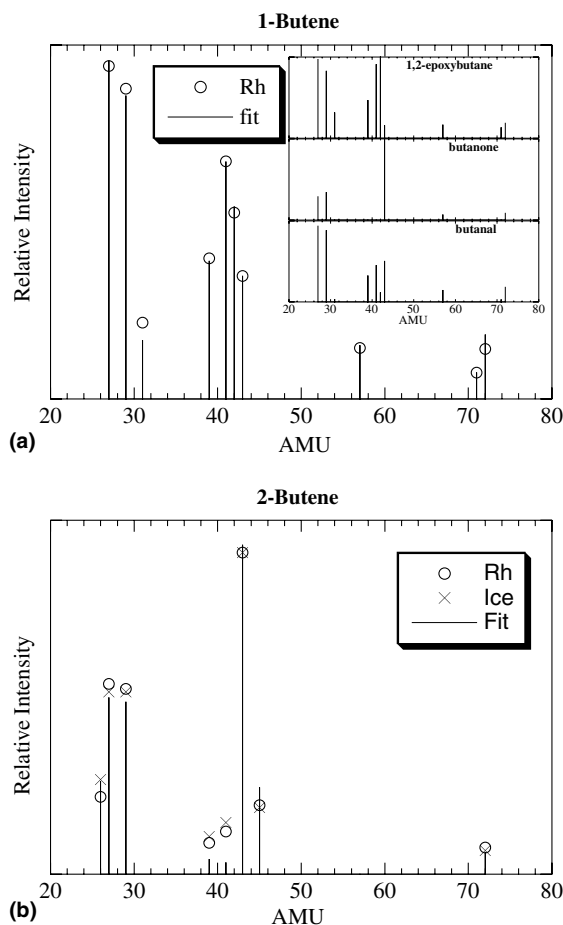


Fig. 1. (a) The results for 1-butene. (b) The results for the 2-butenes. The symbols are the data, and the solid lines are from the least-squares fit (see text). The results shown in (a) were fit with the combination of the three different products whose mass spectra are shown in the inset. In the case of the 2-butenes, the fit is from an average of the results for the Rh(111) and ice-covered surface.

Rh and ice surfaces are compared. With this library of possible products, a least-squares procedure was used to determine the best possible combination of reaction adducts.

## 3. Results and discussion

The masses observed in the detector can be accounted for by a combination of oxygen addition products. At the temperature of these experiments, the products remained adsorbed on the surface, and were only observed in the post-reaction TPD spectra. No detectable  $CO$ ,  $CO_2$ , or  $OH$  was evolved. The relative intensities for the important mass fragments are shown in Fig. 1 for the reaction of 1- and 2-butene adsorbed on both the Rh(111) and the ice surfaces when using the 200-meV O atom beam. For 1-butene, the principal product as determined by the fitting procedure was 1,2-epoxybutane ( $\sim 60$ – $70\%$ ), with the remainder being principally butanal with a trace of butanone. For the 2-butenes (a mixture of *cis*- and *trans*-), the results were fit with a combination of *cis*- and *trans*-2,3-

epoxybutane and butanone. The discrepancy at masses 41 and 43 (see Fig. 1) can be attributed to a trace of 2-methyl-propanal. This is consistent with the results from thick condensed films [7,8]. A crude estimate of the quantity of product can be made by comparing the signal with that from ordered CO and H<sub>2</sub>O adsorbed on clean Rh(111). The result is that there are at most only a few layers of adsorbed product after 20 min exposure.

Before exposure, the chemical composition of the Rh surface can be measured with Auger electron spectroscopy. We observed no reactivity difference between a surface that had been cleaned prior to exposure and after several experiments. However, an initially clean surface quickly acquires some adsorbed carbon. Some of the butenes or the reaction products must partially decompose, so that the reaction is no longer occurring on a clean Rh surface. After repeated experiments with no surface cleaning between runs, the surface showed at most the equivalent of about one monolayer of carbon.

For the ice, we estimate the thickness to be at least 150 Å, estimated by comparing the signal with that of a bilayer of crystalline ice grown on clean Rh(111). At 120 K, the temperature at which the ice was grown, it is almost certainly amorphous, so the surface could be quite rough. The two maxima in the mass 18 TPD spectrum of Fig. 2 are probably due to the conversion of the ice from amorphous to crystalline as the surface is heated [14]. The reaction occurs principally at the surface. This is clearly shown in Fig. 2, where the TPD spectra for masses 27 and 18 after exposure to O(<sup>3</sup>P) and 2-butene are compared. Since most of the addition products are desorbed before any of the H<sub>2</sub>O, they can only be on the surface. The tail and small peak at the higher temperatures may be due to some mixing with the water as the ice surface begins to sublime. Even on the Rh(111) surface, butanone shows a pronounced high-temperature tail.

As already mentioned, the butenes were only transiently adsorbed on the Rh or ice surfaces; none showed up in TPD spectra taken after exposure without any concurrent

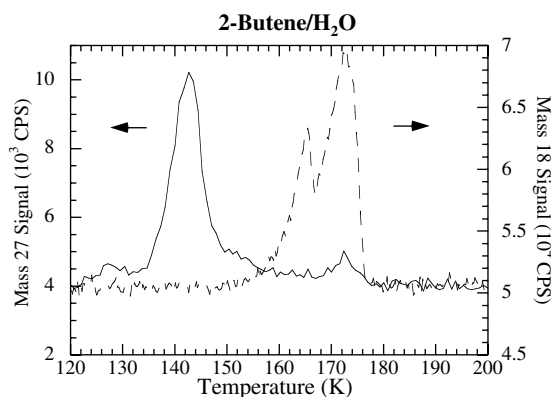


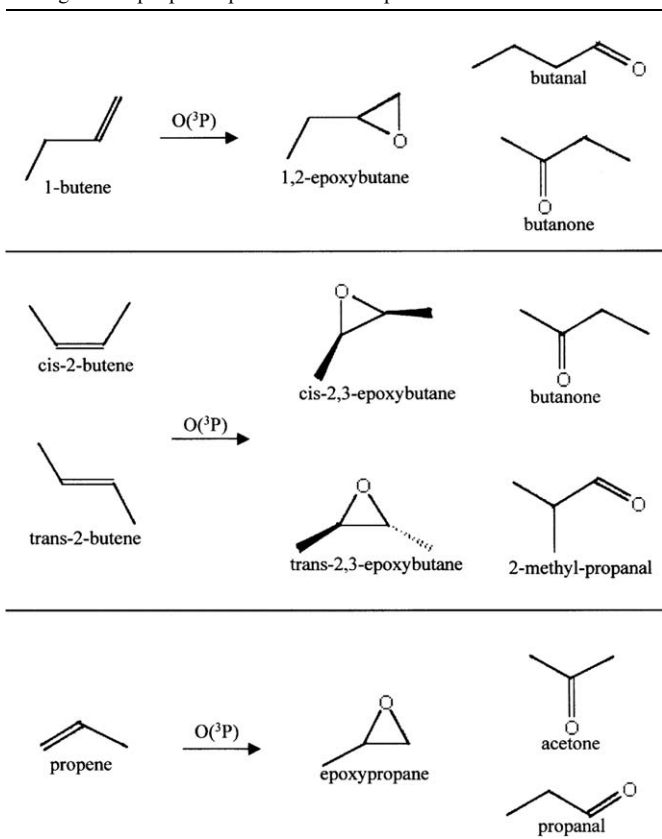
Fig. 2. A comparison of the mass 27 and mass 18 TPD spectra for the 2-butenes reacting with O(<sup>3</sup>P) on amorphous ice, taken at 0.5 K/s. The small feature around 128 K is a small amount of unreacted 2-butene.

O atoms. However, in the case of the 2-butenes, a small amount appeared in the TPD spectra after O(<sup>3</sup>P) exposure. This appears as a small low-temperature feature at ~128 K as shown in the mass 27 spectrum of Fig. 2.

The 2-butenes produced an apparently larger quantity of products than 1-butene, though this is hard to precisely determine due to differences of ionization in the detector. The ice surface produced ~20–30% more than the Rh surface when exposed to the 2-butenes. One possibility is that the softer ice surface better accommodates the incoming molecules, allowing for a longer residence time in which reaction can occur. The rate of production was also investigated for 1-butene on the Rh surface. The exposure time before taking the TPD spectra was varied from 5 min to 1 h with the result that the quantity produced is linearly dependent on the exposure time. We also investigated the reaction of the 2-butenes on the Rh surface using O(<sup>3</sup>P) with a kinetic energy of 66 meV. When corrected for the lower O atom flux of this beam, the results were identical with the beam having the higher kinetic energy. This observation indicates that the reaction mechanism is, at most, only slightly activated (Table 1).

We also investigated the reactions of propene and O(<sup>3</sup>P) (average translational energy 70 meV) on a Au(111) surface. At surface temperatures of ~130 K, only a small amount of propene is adsorbed, probably much less than

Table 1  
Listing of the proposed products for the partial oxidation reactions



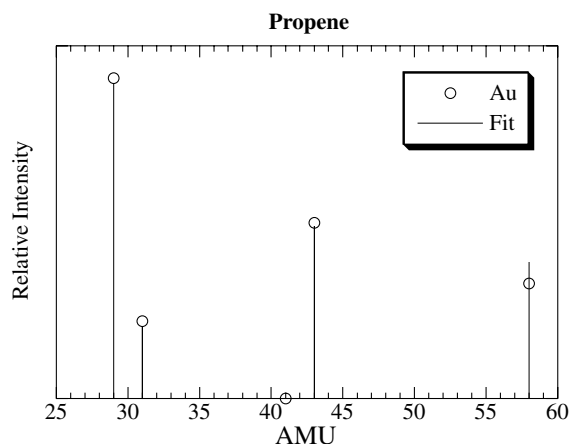


Fig. 3. The results for propene reacting with  $O(^3P)$  on Au(111). The symbols are the data, and the solid lines are from the least-squares fit (see text).

a monolayer; there is no multilayer build-up. When the Au(111) surface is exposed to simultaneous  $O(^3P)$  and propene beams, only partial oxidation products were detected in TPD spectra. Fig. 3 shows the data and fit, indicating that the products are epoxypropane ( $\sim 50\%$ ), with the remainder being about equal amounts of propanal and acetone. As with the case for butene, this is consistent with the results from thick condensed films [7,8].

#### 4. Conclusions

We have examined the reaction of molecular beams of 1- and 2-butene and a beam of  $O(^3P)$  interacting on Rh(111) and ice surfaces at  $T_s \approx 120$  K, and propene and  $O(^3P)$  beams interacting on Au(111) at  $T_s \approx 130$  K. Only addition products were observed, and these remained on the surfaces until heated. The yield is linearly dependent on exposure time and independent of the kinetic energy of the incident  $O(^3P)$  atoms with kinetic energies of 66 and 200 meV (6 kJ/mol and 19 kJ/mol). Under the conditions of these experiments, the alkenes are only transiently adsorbed, and the observed products were formed directly on the metal or ice surface. However, because of similar reaction rates for the 2-butenes on the active Rh(111) and inert ice surfaces, the reactions are not catalyzed by the surface. The substrate does serve to stabilize the products by absorbing the energy liberated from these highly

exoergic reactions. Another channel that is observed in the gas phase is hydrogen abstraction and the liberation of OH. However, the rates for the reaction of  $O(^3P)$  with alkanes, which involves hydrogen abstraction, are 2–3 orders of magnitude less than the reaction with the corresponding alkenes, which involves both abstraction and oxygen addition [11,15]. Also, the activation energy for hydrogen abstraction is greater than for oxygen addition [4]. When the reaction is between  $O(^3P)$  and an alkene both transiently adsorbed on the surface, then oxygen addition should be by far the dominant reaction, particularly at low surface temperatures [16]. That is precisely what has been observed in these experiments.

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