

# Use of Oxygen-18 to Determine Kinetics of Butadiene Epoxidation over Cs-Promoted, Ag Catalysts

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Kinetic isotope effect (KIE) data have been measured using <sup>18</sup>O<sub>2</sub> for butadiene epoxidation over Cs-promoted, supported Ag catalysts. These show that the rate-limiting step for butadiene epoxidation is dissociation of a molecular oxygen species (O<sub>2</sub>)<sup>-1</sup> on a vacant Ag surface site. Comparisons have been made between the experimentally measured KIE values and calculated KIE values for reaction steps (other than O–O dissociation) involving bond-making or bond-breaking steps in which oxygen is involved. In all these instances the calculated KIE values are much lower than the KIE actually observed. This study marks the first instance where <sup>18</sup>O<sub>2</sub> has been used at steady-state olefin epoxidation conditions to confirm the nature of the oxygen active in olefin epoxidation. The O-18 results in this study also directly support the current belief that atomic oxygen, and not a molecular oxygen species, is the active form of oxygen that reacts with olefins to form olefin epoxides. Finally, comparison of the kinetics for butadiene epoxidation with the kinetics for ethylene epoxidation shows that the rate-limiting steps for the two reactions are different. For ethylene epoxidation, the surface reaction between adsorbed ethylene and adsorbed oxygen is considered to be the limiting step, while dissociation of molecular oxygen dissociation is rate limiting for butadiene epoxidation. © 2001 Academic Press

**Key Words:** epoxybutene; oxygen-18; kinetic isotope effect; reaction mechanism; oxygen dissociation; silver catalyst.

## 1. INTRODUCTION

The epoxidation of higher, nonallylic olefins using molecular oxygen has attracted much interest recently (1–8), especially for the case of butadiene epoxidation to form 3,4-epoxy-1-butene (EpB) because of its versatility in preparing myriad chemical intermediates of importance to the fine and specialty chemical markets (9, 10). In addition, because butadiene is the simplest example of a nonallylic olefin other than ethylene, studies of butadiene epoxidation

may provide key insights into the mechanism of ethylene epoxidation. Thus, an investigation of the kinetic parameters for butadiene epoxidation not only improves our understanding of the kinetics for this potentially important reaction, but may also add to our fundamental knowledge of epoxidation of other olefins.

Earlier work by Monnier (1) has shown basic differences between the kinetics of butadiene and ethylene epoxidation. The formation of EpB (EpB is a registered trademark of Eastman Chemical Company) is strongly inhibited by the presence of previously formed EpB. This observation, coupled with the activity and selectivity enhancement effects of Cs<sup>+</sup>, Rb<sup>+</sup>, and Tl<sup>+</sup> promoter salts, which lower the desorption energy of EpB from the promoted Ag surface (1, 11), supports the hypothesis that the desorption of EpB is involved in the rate-determining step (RDS) of epoxybutene formation. Monnier (1) observed that, in the absence of optimized levels of promoter salts, the strongly bound EpB gave low levels of butadiene conversion, low selectivity to EpB, and short catalyst lifetimes (<3–4 h). The addition of promoter salts sufficiently lowered the strength of EpB adsorption to a point that while EpB was still relatively strongly bound and did inhibit the rate of further EpB formation (negative first order in EpB concentration for further EpB formation), the desorption was facile enough that high rates of butadiene conversion and high selectivity to EpB were observed at long catalyst lifetimes. This conclusion is also consistent with the results of Roberts *et al.* (12), who used temperature-programmed desorption methods to study the reaction of saturation coverages of co-adsorbed butadiene and oxygen on Ag(110) surfaces. The authors found that, at temperatures of 400–500 K, a variety of reaction products, including 2,5-dihydrofuran, furan, carbon dioxide, and water were formed; however, epoxybutene was not detected as a reaction product. These results are consistent with the observations of Monnier (1) for butadiene epoxidation over unpromoted, supported Ag catalysts. Addition of different reaction products (2,5-dihydrofuran, epoxybutene, crotonaldehyde, furan, and acrolein) to the reactor feedstream during reaction confirmed that

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epoxybutene was the sole product of butadiene epoxidation, but that the strongly bound EpB underwent many side reactions to give the slate of products observed by Madix. Monnier and Muehlbauer have also reported similar behavior for epoxidation of styrene (13) and norbornene (14) over supported Ag catalysts. In the absence of Cs<sup>+</sup>, Rb<sup>+</sup>, and Tl<sup>+</sup> promoters, only trace amounts of styrene oxide and norbornene oxide were detected as reaction products. Only after promotion were the catalysts highly active and selective for olefin epoxide formation. Earlier work by Cant *et al.* (15) for epoxidation of norbornene over unpromoted Ag catalysts at continuous flow conditions yielded only benzene, CO<sub>2</sub>, and H<sub>2</sub>O as the reaction products, again consistent with the existence of strongly bound norbornene oxide that undergoes decomposition on the Ag surface to form benzene before desorption of norbornene oxide can occur. In related work, however, Roberts and Madix (16), using temperature-programmed desorption methods, found that norbornene oxide did desorb at approximately 310 K from a Ag(110) surface that had been exposed to O<sub>2</sub> and norbornene at 120 K. It should be kept in mind, however, that temperature-programmed methods involve only a single turnover at a surface site, while continuous flow measurements assess catalytic behavior at conditions of multiple turnovers of reactants.

The above body of work clearly suggests that desorption of these higher olefin epoxides is critical and, in the case of butadiene epoxidation, that the desorption of EpB affects the RDS of the reaction. Specifically how the desorption of EpB affects the RDS, however, is not known. In this communication, we present kinetic isotope effect (KIE) data for butadiene epoxidation over Cs-promoted, supported Ag catalysts using <sup>18</sup>O<sub>2</sub> at steady-state reaction conditions. Primary kinetic isotope effects (KIEs) have been experimentally determined and compared to calculated KIE values for different reaction steps involving bond-making or bond-breaking steps in which oxygen is involved. To the best of our knowledge, this is the first instance where <sup>18</sup>O<sub>2</sub> has been used at steady-state olefin epoxidation conditions to determine whether an O-inclusive KIE exists. The closest analogy has been work performed by Bertole and Mims (17), who have used isotope transients (done by switching reactor feed streams from <sup>16</sup>O<sub>2</sub> → <sup>18</sup>O<sub>2</sub>) to investigate the role of subsurface oxygen in ethylene epoxidation on Ag catalysts. The only other reported case in which <sup>18</sup>O<sub>2</sub> has been used to determine whether a KIE existed for catalytic oxidation reactions has been reported by Monnier and Keulks (18). The authors used <sup>18</sup>O<sub>2</sub> at steady-state reaction conditions to confirm that the RDS for propylene oxidation to acrolein at low temperatures (300–350°C) over β-Bi<sub>2</sub>Mo<sub>2</sub>O<sub>9</sub> involved dissociation of adsorbed molecular oxygen. There are several possible explanations why <sup>18</sup>O<sub>2</sub> has not been used for KIE studies: for example, the cost of isotopically pure <sup>18</sup>O<sub>2</sub> and the small magnitude of

oxygen-18 KIE values. Oxygen-18 KIE values are much smaller than those for C–D or D–D bond-making or bond-breaking steps (19). Regardless, with careful design of experiments and the use of highly quantitative inline gas sampling, we show that such experimental studies are not only economical and feasible, but also highly informative with respect to kinetic analysis of the Ag-catalyzed epoxidation of butadiene.

## 2. EXPERIMENTAL

The CsCl-promoted, supported silver catalyst used in this study was prepared using methods that have been described earlier (1, 2). The finished catalyst, containing an optimized level of CsCl promoter, contained 680 ppm Cs based on the total weight of the supported catalyst; the Ag loading was 12% by weight. The catalyst support was fused α-Al<sub>2</sub>O<sub>3</sub> rings, type SA-5562, which were supplied by Norton Corporation. The surface area of the SA-5562 support was 0.7–0.8 m<sup>2</sup>/g with a total pore volume of 0.55 cm<sup>3</sup>/g, and median pore diameter of 7 μm. Using automatic particle counting/measuring software to determine Ag crystallite diameters from scanning electron micrographs, the average Ag particle diameter was calculated to be 0.14 μm, corresponding to a Ag dispersion value of 0.0080. The Ag surface site density was thus calculated to be 5.37 × 10<sup>18</sup> Ag sites/g catalyst based on a hemispherical particle shape. Previous O<sub>2</sub> chemisorption analyses using the method described by Plischke and Vannice (20) for a similar series of CsCl-promoted, Ag catalysts showed that normalized O<sub>2</sub> uptake values for optimal CsCl-promoted catalysts were approximately one-half of the O<sub>2</sub> uptake for the analogous, unpromoted catalyst. Thus, we assume the surface Ag site concentration of the promoted catalyst in this study to be approximately 2.7 × 10<sup>18</sup>/g catalyst.

The kinetic isotope experiments were carried out in a tubular Pyrex reactor with dimensions of 0.6 cm i.d. × 18 cm length (upper half of reactor) and 0.2 mm i.d. × 12 cm length (lower half of reactor) containing a catalyst charge of 0.50 g in the midsection of the tube. The catalyst bed dimensions were approximately 0.6 cm diameter × 2.0 cm in height. Directly above the catalyst, the reactor was packed with ground/sieved inert Dentstone preheat packing. The catalyst sample was also ground and sieved to give particle diameters of 0.4–0.8 mm. The reactor was tightly clad with a 2.5 cm outside diameter (o.d.) aluminum jacket to help ensure a more isothermal catalyst bed. A thermocouple (1.0 mm o.d.) embedded in the middle of the catalyst bed was used to monitor and maintain catalyst temperature. Before catalyst evaluation, the catalyst sample was heated in flowing air *in situ* at 250°C for 2 h. The temperature of the sample was then lowered to 200°C, and the catalyst was allowed to activate and reach steady-state activity (approximately

36 h online) at 200°C in a feed stream of 300 ml (STP)/min containing 9% C<sub>4</sub>H<sub>6</sub>, 18% O<sub>2</sub>, 73% *n*-C<sub>4</sub>H<sub>10</sub> (diluent) plus 2 ppm 2-chlorobutane, which was added as a reaction moderator. Previous work (2) had shown that catalyst activation was accompanied by Cl loss from the surface of the Ag catalyst; both EpB and *n*-C<sub>4</sub>H<sub>10</sub> constantly removed Cl from the Ag surface. The addition of 2 ppm 2-chlorobutane was required to maintain even low Cl levels on the surface of the Ag catalyst. Typical measurable concentrations of Cl by X-ray fluorescence indicated that, at steady-state conditions, the catalyst contained 10–30 ppm of Cl. Catalyst performance was monitored every 2 h throughout the entire run by automatic inline gas sampling injection into a Poraplot Q gas chromatographic column installed in a Hewlett-Packard 5890 Series Gas Chromatograph. Signal collection and integration were carried out using a Hewlett-Packard 3396 Series II computing integrator.

After steady-state activity had been attained at 200°C, the reaction temperature was lowered to 170°C for measurements of the kinetic isotope effects. The overall flow rate to the catalyst was lowered to 60 ml (STP)/min (feed compositions maintained by Tylan FC-260 mass flow controllers) with a feed composition of 17% <sup>16</sup>O<sub>2</sub> (or <sup>18</sup>O<sub>2</sub>), 17% C<sub>4</sub>H<sub>6</sub>, 66% *n*-C<sub>4</sub>H<sub>10</sub>, plus 1 ppm 2-chlorobutane. Two O<sub>2</sub> mass flow controllers (Tylan FC-260) were used for the KIE experiments. One flow controller was connected to a pressurized lecture bottle of <sup>18</sup>O<sub>2</sub> (MSD Isotopes, 97.5% <sup>18</sup>O<sub>2</sub>) and the other to a high pressure supply of research grade (99.99% purity), high pressure <sup>16</sup>O<sub>2</sub>. The two oxygen feed sources were hooked to a four-way Valco valve, which permitted rapid step switches in the oxygen feed supply from <sup>16</sup>O<sub>2</sub> to <sup>18</sup>O<sub>2</sub> (or vice versa) to the reactor, with the other oxygen flow going directly either to vent or shut-off. This rapid change in oxygen feed sources maintained the previously established steady-state activity.

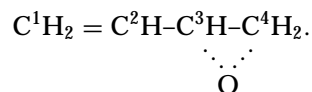
Before addition of the isotopic oxygen, the catalyst was allowed to reach steady state at the new reaction conditions. At a reaction temperature of 170°C and the feed compositions stated above, butadiene and oxygen conversions were approximately 2.8% and 1.5%, respectively; thus, differential conversions of both butadiene and oxygen were maintained throughout all KIE experiments. Selectivity to EpB was 99%, with byproducts limited to CO<sub>2</sub>/H<sub>2</sub>O. The high selectivity to EpB was not unexpected at 170°C, since the apparent activation energies for EpB and CO<sub>2</sub> formation are 26.4 and 45.6 kcal/mol, respectively, thus favoring higher selectivities at lower reaction temperatures (1). Even in this low temperature region, the turnover frequency to epoxybutene was 0.10 s<sup>-1</sup>. A reaction temperature of 170°C was selected for the KIE experiments, since the theoretical magnitudes of KIE values are larger at lower temperatures.

The oxygen sequence used during measurement of KIE values was <sup>16</sup>O<sub>2</sub>-<sup>18</sup>O<sub>2</sub>-<sup>16</sup>O<sub>2</sub>. This sequence was repeated four times to give four independent determinations of the

KIE for O-18. The flow of <sup>18</sup>O<sub>2</sub> was maintained for 60 s before online gas chromatography (GC) analysis of the reaction products was conducted. The dead volume between the <sup>18</sup>O<sub>2</sub> source (four-way valve) and the GC sample loop was approximately 5 ml, meaning that essentially 12 gas turnovers in the reactor occurred before a GC sample was taken. The gas turnover efficiency was independently confirmed by using CH<sub>4</sub> as a tracer for 60 s in place of the O<sub>2</sub> flow during experimental setup. Constant CH<sub>4</sub> concentrations in the feed were reached after approximately 10 s online, indicating that <sup>18</sup>O<sub>2</sub> flow for 60 s should give valid steady-state data after 60 s online.

### 3. RESULTS AND DISCUSSION

The kinetic isotope results for epoxybutene formation are summarized in Table 1. The average <sup>16</sup>O<sub>2</sub>/<sup>18</sup>O<sub>2</sub> rate ratio for the four different <sup>16</sup>O<sub>2</sub>-<sup>18</sup>O<sub>2</sub>-<sup>16</sup>O<sub>2</sub> sequences is 1.120 with a standard deviation of 0.020. The magnitude of the KIE clearly indicates that a surface reaction involving oxygen bond-breaking or bond formation is involved in the RDS of epoxybutene formation. There are several possible sources for the O-18 isotope effect. The most straightforward is dissociation of chemisorbed molecular oxygen; the others involve C–O bond formation with butadiene intermediates, shown schematically below:



In this scheme, bond formation between C<sup>3</sup> and O and C<sup>4</sup> and O are considered. To determine the source of the KIE shown in Table 1, KIE values were calculated for the different possible reaction steps using the method detailed by Melander (21). In this method, it is assumed that differences in zero-point energy contributions to the reactant and transition state partition functions between isotopes are negligible except in the direction of the reaction coordinate.

TABLE 1

Experimental KIE Values for Epoxybutene Formation at 170°C over CsCl-Promoted, Supported Ag Catalyst

Sequence no. ( <sup>16</sup> O <sub>2</sub> - <sup>18</sup> O <sub>2</sub> - <sup>16</sup> O <sub>2</sub> )	<i>k</i> <sub>O-16</sub> / <i>k</i> <sub>O-18</sub>
1	1.143
2	1.113
3	1.095
4	1.127
Average	1.120 ± 0.020

Note. Average KIE and standard deviation are also shown.

TABLE 2

Calculation of Theoretical KIE Values at 170°C for O–O Bond Dissociation of Different Molecular O<sub>2</sub> Species<sup>a</sup>

Reference	O <sub>2</sub> species	<sup>16</sup> O– <sup>16</sup> O stretch (cm <sup>-1</sup> )	<sup>18</sup> O– <sup>18</sup> O calculated (cm <sup>-1</sup> )	$k_{O-16}/k_{O-18}$
22	O <sub>2</sub> (gas)	1580	1489	1.157
23	O <sub>2</sub> <sup>-</sup> (KO <sub>2</sub> )	1140	1074	1.117
24	O <sub>2</sub> <sup>-</sup> (AgO <sub>2</sub> )	1081	1019	1.114
25	O <sub>2</sub> <sup>2-</sup> (Na <sub>2</sub> O <sub>2</sub> )	766	722	1.088
26	O <sub>2</sub> <sup>2-</sup> (RCO <sub>2</sub> PdOO- <i>t</i> -Bu)	860	810	1.095
27	O <sub>2</sub> <sup>2-</sup> (Ag(001))	678	645 <sup>b</sup>	1.070

<sup>a</sup> The chemical composition of the O<sub>2</sub> species is in parentheses.

<sup>b</sup> Measured experimentally using adsorbed <sup>18</sup>O<sub>2</sub>.

For this case, the reaction coordinate corresponds to the stretching mode of the bond that is going to be cleaved or formed in the reaction. Because the transition state is assumed to have one fewer degree of freedom (in the direction of the reaction coordinate), the KIE can be approximated using only the stretching frequencies for the <sup>16</sup>O and <sup>18</sup>O-labeled reactant molecules. Before KIE values were measured, calculations were made to determine population of the first excited vibrational state ( $v = 1$ ) at reaction conditions. The population of the first excited state was found to be negligible. Calculated KIE values for dissociation of various molecular oxygen species are summarized in Table 2. The bond order of the O–O linkage, and hence the stretching frequency, decreases as the number of electrons in the  $\pi^*$  antibonding orbital increases. The magnitude of the experimental KIE values in Table 1 is in very good agreement with the values in Table 2 for dissociation of an O<sub>2</sub><sup>-</sup> species at the RDS. This is consistent with most O–O bond cleavage mechanisms, which involve population of the  $\pi^*$  orbitals to lower the O–O bond order, and thus decrease the stability of the O<sub>2</sub> molecule. Kinetic isotope effects have also been calculated in Table 2 for three different peroxo (O<sub>2</sub><sup>2-</sup>) species. The experimental KIE values in Table 1 are considerably larger than the calculated values for these species in Table 2, meaning that the electronic structure of the O–O species at the transition state more closely resembles O<sub>2</sub><sup>-</sup> than O<sub>2</sub><sup>2-</sup>. This suggests that the peroxo species identified as the stable adsorbed form of O<sub>2</sub> from oxygen chemisorption on Ag surfaces is not the active species in molecular oxygen dissociation (27). The Pd(II) *t*-butyl peroxide carboxylate species in Table 2 can also be used to approximate the reaction intermediate if molecular oxygen is the active oxygen species during olefin epoxidation. The calculated KIE is again sufficiently lower than the experimental values to support the contention that atomic oxygen, rather than molecular oxygen, is the active oxygen during electrophilic addition to the C=C bond. This is discussed further at a later point.

To confirm that dissociation of an O<sub>2</sub><sup>-</sup> species is the source of the experimentally observed KIE and is thus the RDS

for EpB formation, it is necessary to calculate theoretical KIEs for other individual steps in the overall epoxidation mechanism. Certainly one important mechanistic step is the surface reaction of adsorbed atomic oxygen with butadiene. Although this process has not yet been explored theoretically, it is possible to estimate a maximum KIE for this step by considering the reverse reaction. In previous ultra-high vacuum (UHV) studies on a Ag(110) single crystal (7), the strongly adsorbed state of EpB has been identified as a surface oxametallacycle. The oxametallacycle structure was identified by the excellent agreement between experimental and density functional theory (DFT)-calculated vibrational spectra. Because it has been verified experimentally, this DFT model gives us a framework for calculation of *approximate* KIEs associated with reactions of this intermediate. These calculations are particularly useful in illustrating the magnitude of various possible KIE values. Density functional theory calculations for the oxametallacycle have predicted a C<sup>4</sup>–O stretching frequency (potentially corresponding to the reverse, oxygen abstraction reaction) of 844 cm<sup>-1</sup>. To estimate the KIE associated with this reaction step, frequency calculations have also been performed for an <sup>18</sup>O-labeled oxametallacycle intermediate using the previously described methods of Medlin *et al.* (6). The frequency of this mode is shifted to 814 cm<sup>-1</sup> for the <sup>18</sup>O-labeled oxametallacycle. Thus, this analysis predicts a maximum KIE of 1.058, well below that observed in this study. In fact, the KIE for C–O bond formation would probably be even lower than 1.058, since bond-breaking steps are typically associated with larger KIE values than are seen for bond-formation steps (20).

In UHV experiments on Ag(110) described previously, the strongly adsorbed oxametallacycle intermediate has been shown to react via ring closure (O–C<sup>3</sup> bond formation) to produce EpB (7). Therefore, this step must also be considered as potentially responsible for the experimentally observed KIE. As reported previously, DFT calculations have identified a vibrational mode at 442 cm<sup>-1</sup> that corresponds to the reaction coordinate for ring closure of the oxametallacycle to form EpB. Similar calculations for the <sup>18</sup>O-labeled oxametallacycle reveal that the frequency of this mode is shifted downward to 432 cm<sup>-1</sup>, yielding a maximum theoretical KIE of 1.027. This KIE is far below that observed for the steady-state butadiene epoxidation reaction, indicating that oxametallacycle ring closure is not rate limiting.

The conclusion that oxametallacycle ring closure reaction to EpB is not the RDS can also be reached by considering the *overall* reaction coordinate for butadiene epoxidation. A basic schematic of this reaction coordinate is shown as Fig. 1. Previous calculations (11), using the methods described by Seaton *et al.* (28) have indicated that butadiene epoxidation is exothermic by 22 kcal/mol at reaction temperature (i.e., EpB is more stable than the reactants by 22 kcal/mol). Temperature-programmed desorption

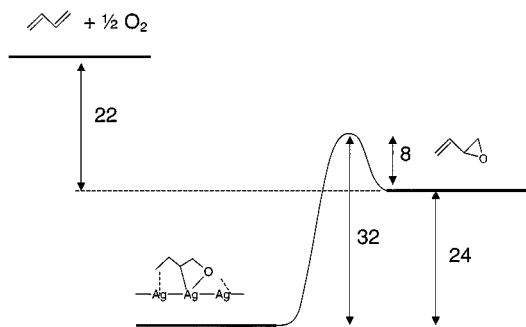


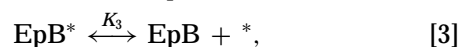
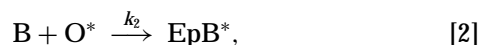
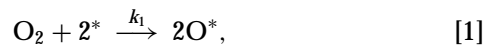
FIG. 1. Reaction coordinate for butadiene epoxidation. Heat of reaction and activation energy values are given in kcal/mol.

experiments have been used to measure the forward and reverse activation energies for oxametallacycle ring closure to form EpB (7). As shown in Fig. 1, these  $E_a$  values are 32 and 8 kcal/mol, respectively. Thus, the oxametallacycle intermediate is more thermodynamically stable than EpB by approximately 24 kcal/mol. Moreover, the transition state for EpB formation from the oxametallacycle intermediate is actually lower in energy than the reactants, butadiene and oxygen. In other words, even though the activation energy for oxametallacycle ring closure is a relatively high 32 kcal/mol, this individual step is still overall downhill in energy from the reactants. This step will therefore be rapid, and a steady-state equilibrium between gas-phase EpB and surface oxametallacycles will be established. This analysis suggests that the RDS of butadiene epoxidation must involve the activation of the reactants, consistent with the hypothesis that O–O bond cleavage is rate limiting. Because of the strongly adsorbed nature of the oxametallacycle intermediate, however, the equilibrated ring closure step can still play an important role in the overall kinetics; this point is considered in detail below.

One further consideration is that desorption of molecular epoxybutene from the Ag surface is the rate-limiting step. While it is difficult to envision the nature of the bonding between adsorbed, molecular EpB and Ag, the strong kinetic inhibition by EpB is an indication that some form of EpB, or EpB precursor, is strongly bound to the Ag surface. From HREELS studies (7) of EpB adsorbed on Ag(110), a shoulder at  $220\text{ cm}^{-1}$  has been identified that we attribute to the Ag–O stretch between Ag and adsorbed EpB. This assignment appears reasonable, since stretching frequencies in the  $200\text{--}300\text{ cm}^{-1}$  range would be expected for O–Ag vibrations (29). If we use  $220\text{ cm}^{-1}$  as the Ag–O vibrational frequency for O-16 labeled EpB, the stretching frequency is shifted to  $218\text{ cm}^{-1}$  for O-18 labeled epoxybutene, which gives a theoretical KIE of 1.009 at  $170^\circ\text{C}$ . This calculated KIE is again much lower than the measured value. It should also be noted that the transition state for molecular adsorption of EpB would not be expected to be significantly higher in energy than gas-phase EpB. Based on the reasoning cited

above, this provides a further indication that molecular EpB desorption is not involved in the RDS.

After consideration of all the possible sources of O-18 kinetic isotope effects for butadiene epoxidation, these theoretical analyses indicate that the only reaction step that can result in an isotope effect on the order of 1.12 is the dissociation of molecular oxygen, which apparently exists as  $\text{O}_2^-$ , at the RDS of EpB formation. To reconcile the strong kinetic inhibition effect of EpB with the conclusion that dissociation of molecular oxygen is the RDS for formation of EpB, we can suggest the three (out of several) elementary surface reaction steps,



where B is shorthand for butadiene and an asterisk represents a surface site. In this model, oxygen dissociation and butadiene surface reaction are considered irreversible steps, whereas EpB desorption is considered to be at equilibrium. Equilibrium adsorption/desorption of EpB is consistent with the kinetic analysis performed earlier (1), whereby variable amounts of EpB were added to the reactor feedstream during reaction to determine the negative first-order kinetic dependency in EpB concentration for additional EpB formation. That EpB adsorption/desorption was an equilibrium process was verified when EpB was removed from the reactor feed and reaction rates were fully restored. Making use of the equilibrium relationship between strongly adsorbed and gas-phase EpB, we write an expression for the concentration of sites on which EpB is adsorbed:

$$[\text{EpB}^*] = \frac{[\text{EpB}][^*]}{K_3}. \quad [4]$$

After some simple algebraic manipulation, application of the pseudo-steady-state approximation yields expressions for the rate of oxygen dissociation,

$$r = 2k_1[\text{O}_2][^*]^2, \quad [5]$$

$$r = 2k_1[\text{O}_2]L^2 \left( \frac{K_3}{K_3 + [\text{EpB}]} \right)^2, \quad [6]$$

where  $L$  represents the total number of surface sites and bracketed terms indicate species concentrations. Because EpB is strongly adsorbed on the surface, we assume that sites with adsorbed EpB are the dominant surface species (i.e.,  $[\text{EpB}^*] \gg [^*]$ ). It follows from Eq. [4] that  $[\text{EpB}] \gg K_3$ , which leads to the following proportionality for the rate:

$$r \propto \frac{k_1[\text{O}_2](K_3)^2}{[\text{EpB}]^2}. \quad [7]$$

Of course, this is an approximate expression since it does not include the other kinetic parameters that have been discussed earlier (1), namely the kinetic dependency of butadiene and the negative reaction orders in  $\text{CO}_2$  pressure. The goal here is not to attempt to write a complete rate expression that satisfies all observed kinetic parameters, but to reconcile the strong kinetic inhibition by EpB within the framework of dissociation of molecular oxygen as a RDS for EpB formation. Clearly, although the strongly adsorbed state of EpB does not affect the RDS in a direct way, it can still have a strong effect on the kinetics, as demonstrated by the denominator of Eq. [5].

The O-18 results in this study directly support the conclusion that atomic oxygen (16, 30–32), and not a molecular oxygen species, is the active form of oxygen that reacts with olefins to form olefin epoxides. The very high selectivities for EpB formation observed in this study (99%) and in earlier work (1, 2) (94–96%) support the assignment of atomic oxygen as the active oxygen species for butadiene epoxidation. If we use the argument of Sachtler *et al.* (33), commonly known as the 6/7 rule for ethylene oxide formation which states that the selectivity for ethylene oxide formation cannot exceed 6/7, or 85.7%, if molecular oxygen is the active oxygen for epoxidation, then the rule for butadiene epoxidation becomes 11/12 for molecular oxygen. Clearly, the selectivity values cited above for EpB formation are much higher than 11/12, or 91.7%, indicating that molecular oxygen is not the active oxygen that electrophilically adds to the C=C bond during epoxide formation. This study marks the first time that direct evidence has been obtained under steady-state conditions to confirm the nature of the oxygen active in olefin epoxidation. In addition, comparison of the kinetics for butadiene epoxidation with the kinetics for ethylene epoxidation shows that the rate-limiting steps for the two reactions are different. For ethylene epoxidation, the surface reaction between adsorbed ethylene and adsorbed oxygen is considered to be the limiting step (32, 34), while we have shown that molecular oxygen dissociation is rate limiting for butadiene epoxidation. This may largely reflect the significant differences in stability of the oxametallacycle intermediates calculated for the two epoxidation processes (6, 7) and the resulting differences in the occupancy of surface sites by these intermediates under reaction conditions. Furthermore, the similar promoter requirements for styrene (13) and norbornene (14) epoxidation and the existence of strong inhibition effects of both epoxide products on these reactions also suggest that the RDS for epoxidation of these olefins is very likely molecular oxygen dissociation as well. In fact, it is possible that of all the olefins capable of being selectively epoxidized by  $\text{O}_2$  using silver catalysts, the epoxidation of ethylene is the reaction that is different from that of other olefins. If so, this is somewhat ironic, since almost all of our understanding to date regarding olefin epoxidation using  $\text{O}_2$  and Ag catalysts is based on epoxidation of ethylene.

#### 4. CONCLUSIONS

Kinetic isotope effect data using  $^{18}\text{O}_2$  for butadiene epoxidation over Cs-promoted, supported Ag catalysts have been experimentally determined to show that the rate-determining step for butadiene epoxidation is dissociation of a molecular oxygen species ( $\text{O}_2$ )<sup>-1</sup> on a vacant Ag surface site. As confirmation, the experimentally obtained KIE values have also been compared to calculated KIE values for other reaction steps (other than O–O dissociation) involving bond-making or bond-breaking steps in which oxygen is involved. In all these instances the calculated KIE values are much lower than the KIE actually observed. To the best of our knowledge, this is the first instance where  $^{18}\text{O}_2$  has been used at steady-state olefin epoxidation conditions to confirm the nature of the oxygen active in olefin epoxidation.

The O-18 results in this study also directly support the conclusion that atomic oxygen, and not a molecular oxygen species, is the active form of oxygen that reacts with olefins to form olefin epoxides. Finally, comparison of the kinetics for butadiene epoxidation with the kinetics for ethylene epoxidation shows that the rate-limiting steps for the two reactions are different. For ethylene epoxidation, the surface reaction between adsorbed ethylene and adsorbed oxygen is considered to be the limiting step, while dissociation of molecular oxygen is rate limiting for butadiene epoxidation.

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