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Deuterium Kinetic Isotope Effects in Butadiene Epoxidation over Unpromoted and Cs-Promoted Silver Catalysts

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Selectively deuterium-labeled isotopomers of 1,3-butadiene ($CD_2CDCDCD_2$, $CD_2CHCHCD_2$, and $CH_2CDCDCH_2$) have been used as feed reactants to study kinetic isotope effects (KIEs) in the epoxidation of butadiene over both unpromoted and Cs-promoted catalysts. On unpromoted catalysts, the rate of formation of the epoxide product, 3,4-epoxy-1-butene (EpB), is increased relative to that for unlabeled butadiene for the butadiene isotopomers labeled on the terminal carbon atoms. This indicates that EpB formation is characterized by an inverse KIE that is caused by a primary KIE in the rate of the combustion reaction and also demonstrates that combustion is initiated by cleavage of a terminal C–H bond. These KIE phenomena can be explained by a reaction mechanism in which both partial and complete oxidation products are produced from a common C_4H_6O(ads) surface intermediate. The measured KIEs for the reaction over the Cs-promoted catalyst are also consistent with this mechanism. Comparisons between KIE measurements in ethylene and butadiene epoxidation are discussed, and links with surface science studies of C_4H_6O oxametallacycle reactions are established.

Key Words: **deuterium isotope effect; butadiene oxidation; olefin epoxidation; epoxybutene; silver catalyst; epoxidation kinetics.**

INTRODUCTION

The recent discovery of a selective catalyst for the epoxidation of 1,3-butadiene to 3,4-epoxy-1-butene (EpB)[2] (1) has raised some interesting questions about the mechanism of epoxidation reactions. Although epoxidations of both ethylene and butadiene are carried out over silver catalysts, the catalyst for the latter incorporates a much higher loading of the Cs promoter (2). Differences in the measured kinetics within each of these processes also suggest that the relative rates of various elementary steps for these two processes may be different. In other words, the rate-determining steps may be different in each case. By performing comparative studies of ethylene and butadiene epoxidation, it may be possible to obtain a better understanding of the mechanism for silver-catalyzed olefin epoxidations.

One useful method for probing the reaction mechanism is the measurement of kinetic isotope effects (KIEs). Cant and Hall (3) previously studied the silver-catalyzed epoxidation of unlabeled and deuterium-labeled ethylene. They observed a sharp *enhancement* in the rate of ethylene oxide (EO) production when C_2D_4 was used as the reactant. This result seems somewhat surprising, since deuterium kinetic isotope effects are normally associated with a *decrease* in rate for D-labeled compounds. However, Cant and Hall were able to interpret their results in terms of a mechanism in which both ethylene oxide and CO_2 were generated from a common surface intermediate. Under this mechanism, the rate of epoxide production was increased due to an increase in the selectivity to EO. In the present work, we report results from the study of KIEs in the butadiene epoxidation reaction for three deuterium-labeled butadiene reagents: $CH_2CDCDCH_2$, $CD_2CHCHCD_2$, and C_4D_6. These results are then compared to those obtained for the ethylene epoxidation process in order to understand them in terms of a common mechanism for olefin epoxidation.

EXPERIMENTAL

Experiments were conducted in an atmospheric pressure flow reactor system equipped with on-line sampling, similar to systems described previously (4). Standard feed conditions consisted of 9 mol% butadiene and 18% oxygen in a helium diluent, with a total flow of 50–60 standard cubic centimeters per minute (sccm). A temperature-controlled furnace was used to maintain a steady reaction temperature, which was measured via a thermocouple inserted into a thermal well in the catalyst bed. For the KIE experiments, a switching valve (Valco Valves) system was used to switch the flow between the unlabeled and labeled butadiene. The isotopes were introduced into the system using a microprocessor-controlled and well-calibrated syringe pump (Harvard Apparatus, Model 44 Infusion Pump); all

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[2] EpB is a registered trademark of Eastman Chemical Company.

TABLE 1

Kinetic Isotope Effects in Butadiene Epoxidation on an Unpromoted Catalyst

Product	Selectivity[a] (C_4H_6)	TOF, s^{-1} (C_4H_6)	$CH_2CDCDCH_2$ (r_D/r_H)	$CD_2CHCHCD_2$ (r_D/r_H)	$CD_2CDCDCD_2$ (r_D/r_H)	r_D/r_H SD[b]
EpB	26.2%	6.50×10^{-4}	1.01	1.38	1.36	0.02
CO_2	68.6%	1.71×10^{-3}	0.98	0.95	0.96	0.03
Furan	3.3%	8.08×10^{-5}	1.22	1.10	1.38	0.02
Crotonaldehyde	1.6%	3.87×10^{-5}	0.77	0.78	0.68	0.09

[a] Reactor bed temperature = 270°C, butadiene conversion = 1.1%.

[b] The standard deviation represents the *maximum* standard deviation of the 3 r_D/r_H columns.

other components were admitted through mass flow controllers (Tylan Corporation, Model FC-260). Butadiene-2,3-d_2, butadiene-1,1,4,4-d_4, and butadiene-d_6 were obtained from CDN isotopes, and had isotopic purities >98%.

Unpromoted and Cs-promoted Ag/α-Al_2O_3 catalysts were prepared and characterized via previously described methods (5). Cesium chloride was used as the promoter salt for the promoted catalyst. The silver loadings for the unpromoted and promoted catalysts were 13.4 and 12.0%, respectively. Scanning electron microscopy (SEM) was used to determine the distribution of Ag particles on the catalysts. Using automatic particle counting/measuring software to determine Ag crystallite diameters from the scanning electron micrographs, the average Ag particle diameters were calculated to be 0.11 and 0.14 μm for the unpromoted and promoted catalysts, respectively. Assuming hemispherical Ag particles, the Ag surface site densities were thus calculated to be 8.05×10^{18} Ag sites/g catalyst and 5.37×10^{18} Ag sites/g catalyst, respectively, for the unpromoted and promoted catalysts. Previous O_2 chemisorption analyses (5) for a similar series of CsCl-promoted Ag catalysts showed that normalized O_2 uptake values for optimal CsCl-promoted catalysts were approximately one-half of the O_2 uptake for the unpromoted catalyst at comparable Ag loadings. Thus, we assume the surface Ag site concentration of the promoted catalyst in this study to be approximately 2.7×10^{18}/g catalyst. These values for Ag site densities were used for the calculation of turnover frequencies (TOFs) for EpB and CO_2 formation. Both catalysts were sieved to 18/25 mesh and loaded above a coarse frit in the Pyrex reactor. Catalyst loadings of 2.00 and 1.00 g of catalyst were used for experiments with unpromoted and promoted catalysts, respectively. Catalysts were calcined in a flowing stream of 20% O_2 in He at 250°C for 2 h before being brought on line.

RESULTS AND DISCUSSION

After bringing the catalyst on stream at 200°C, the activity of the unpromoted catalyst for epoxidation of butadiene dropped dramatically over a period of 1–2 h. This behavior has been observed previously, and has been attributed to site blocking by a "strongly bound" EpB state (2) that will be referred to here as C_4H_6O(ads). After approximately 2 h on stream, a low but steady-state activity was observed. In order to obtain a quantifiable product yield, the reaction temperature was set at 270°C to give a steady-state butadiene conversion of 1.1%. The first three columns in Table 1 show the product distribution and rates of formation under these reaction conditions. Carbon dioxide is the major reaction product, followed by EpB, furan, and crotonaldehyde. Clearly, after a relatively short time onstream, the unpromoted silver catalyst is neither highly active nor selective for butadiene epoxidation.

In order to determine the influence of butadiene partial pressure on the reaction kinetics, the butadiene feed mole fraction was varied between 4.5 and 18.0% holding all other variables constant. Figure 1 depicts a logarithmic plot of the rate of formation of each product as a function of the butadiene mole fraction. If one assumes power rate law kinetics, the reaction order in butadiene can be determined from the slope of each data set on this plot. As shown in

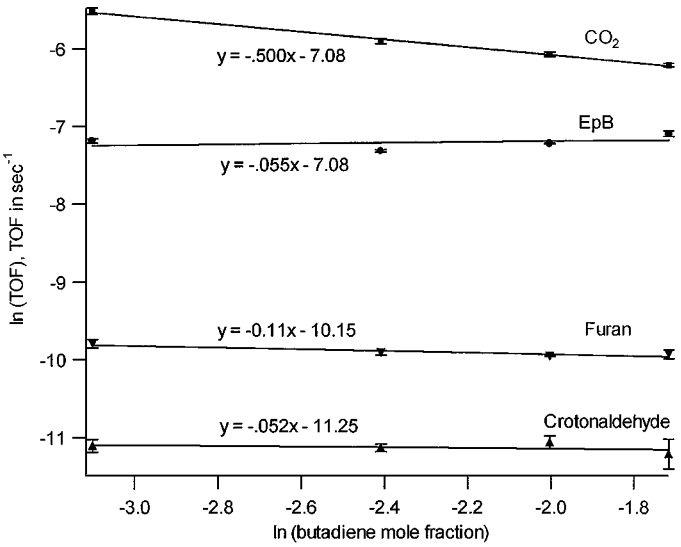
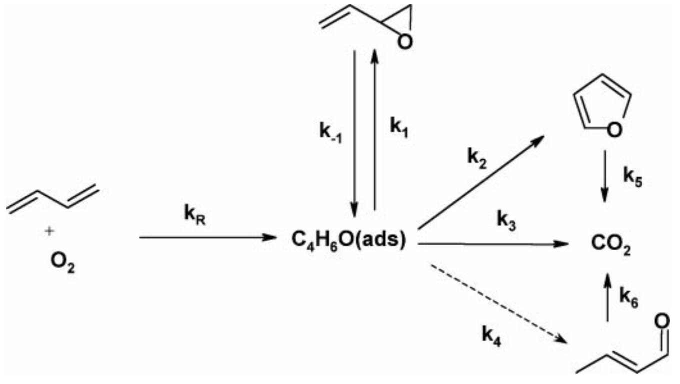


FIG. 1. Power rate law plot for the rate of product formation as a function of butadiene partial pressure.

Fig. 1, the rates of formation of all the partial oxidation products (EpB, furan, and crotonaldehyde) are nearly independent of butadiene partial pressure; CO_2 formation, however, has an apparent order of −0.5 with respect to butadiene. Thus, increasing the mole fraction of butadiene inhibits the combustion process without substantially affecting the rate of formation of other oxidation products. One possible explanation for this result is that increased butadiene adsorption on the catalyst may decrease the coverage of available surface oxygen responsible for deep oxidation. Further studies are necessary, however, to confirm this hypothesis.

The results of experiments conducted with deuterium-labeled butadiene are summarized in Table 1, columns 4–7. The observed KIE values are reported as rate ratios (r_D/r_H), i.e., the rate of formation of each product from the labeled butadiene relative to the rate of formation of that product from butadiene-d_0. The rates of formation of EpB and furan are characterized by having *inverse* isotope effects, whereas the rates of formation of CO_2 and crotonaldehyde undergo the more usual decrease in rate with isotopic substitution. These results are similar to those observed by Cant and Hall for ethylene epoxidation, in which a large inverse KIE for ethylene oxide and a smaller normal effect for CO_2 were observed (3). As demonstrated by Cant and Hall, KIE values of this type can be explained by a mechanism in which multiple products arise from a common reaction intermediate.

To explain the experimental data, we propose the butadiene epoxidation mechanism shown in Scheme 1. The central feature of this mechanism—namely, that EpB and CO_2 are produced from a common surface intermediate—is directly analogous to the scheme proposed by Cant and Hall for ethylene epoxidation. This mechanism is also consistent with studies of EpB adsorption on model silver surfaces. It has been shown that EpB adsorbs on the Ag(110) surface (in a step associated with rate constant k_{-1} in Scheme 1) to form a strongly bound C_4H_6O(ads) oxametallacycle intermediate (6, 7). This oxametallacycle intermediate reacts primarily via the reverse reaction (with rate constant k_1) to regenerate EpB. Small amounts of 2,5-dihydrofuran (2,5-DHF) are also produced on the reduced silver surface during butadiene epoxidation (2). Under the oxidative conditions associated with the butadiene epoxidation reaction, 2,5-DHF rapidly undergoes allylic oxidation to form furan (2); therefore, we conclude that furan is also produced from the common reaction intermediate. Since previous studies have shown that 2,5-DHF does not adsorb on model silver surfaces to form a stable surface oxametallacycle (8), the reaction described by rate constant k_2 is taken to be irreversible.



SCHEME 1. Proposed mechanism for butadiene oxidation.

It is possible that crotonaldehyde is also produced from the common C_4H_6O(ads) intermediate, but the reaction pathway for crotonaldehyde production cannot be deduced from the studies carried out to date. There is no evidence from our surface science studies that crotonaldehyde can be produced from reactions of surface oxametallacycles. Furthermore, the observed KIEs for crotonaldehyde formation are consistent with any mechanism that requires C–H scission in the rate-determining step. Thus, it is possible that crotonaldehyde is formed from the series reaction of another product. Studies are underway to investigate the reaction of C_4H_6O oxametallacycles on oxygen-covered Ag(110) in order to more fully evaluate the mechanism of butadiene epoxidation by determining whether furan, CO_2, and crotonaldehyde are reaction products on the oxidized surface.

The mechanism proposed in Scheme 1 can be used to qualitatively explain the essential features of the isotope effects reported in Table 1. Because further oxidation of the C_4H_6O(ads) intermediate involves C–H bond cleavage, the rate constants for oxidation ($k_{3–6}$) should *decrease* for deuterium-labeled butadiene. The decrease in these rate constants will result in an increase in the concentration of C_4H_6O(ads), which will therefore *increase* the rate of EpB formation. The increase in the C_4H_6O(ads) concentration can also explain the relatively small KIEs observed for CO_2; i.e., although deuterium labeling decreases the rate constant for combustion, k_3, this decrease is nearly offset by the increase in C_4H_6O(ads) concentration.

In their studies of ethylene and propylene epoxidation, Cant and Hall (3) present a series of rate equations derived from the pseudo-steady-state approximation (PSSA) for the common intermediate. From these rate equations, the authors determine KIEs in terms of rate constants for individual mechanistic steps. Neglecting the rate of formation of furan and crotonaldehyde for simplicity (low TOF values in Table 1), a completely analogous treatment (the reader is referred to Ref. (3) for the details) yields

$$r_1 = k_1[C_4H_6O(\text{ads})] - k_{-1}P_{\text{EpB}} \quad [1]$$

for the rate of formation of EpB, where P_{EpB} is the partial pressure of EpB. The concentration of the common surface intermediate, $[C_4H_6O(ads)]$, is evaluated using the PSSA to be

$$[C_4H_6O(ads)] = \frac{k_{-1}P_{\mathrm{EpB}} + k_{\mathrm{R}}P_{O_2}P_{C_4H_6}}{k_1 + k_3}, \qquad [2]$$

where P_{O_2} and $P_{C_4H_6}$ are the partial pressures of oxygen and butadiene, respectively. In their treatment, Cant and Hall (3) neglect the rate of reverse reaction for epoxide formation (i.e., assume k_{-1} is negligible); following this procedure leads to the following expression for the inverse KIE for EpB production at steady state:

$$\frac{r_{1\mathrm{D}}}{r_{1\mathrm{H}}} = \frac{k_1 + k_{3\mathrm{H}}}{k_1 + k_{3\mathrm{D}}}. \qquad [3]$$

Here, rate constants expected to be affected by deuterium labeling are denoted with a subscript D or H. Based on the selectivity data in Table 1, we estimate that $k_{3\mathrm{H}} = 2.6\,k_1$ for unlabeled butadiene, and we also follow the common assumption that $k_{3\mathrm{H}} = 2k_{3\mathrm{D}}$ (10) for reactions limited by C–H bond cleavage. From Eq. [3], this yields a predicted maximum inverse KIE of approximately 1.6, significantly above that reported for any of the isotopomers in Table 1.

However, the PSSA treatment is probably not as appropriate in this case (in comparison to the studies of Cant and Hall) for several reasons. First, butadiene epoxidation is a much more complex reaction, with a broader array of pathways and products, than the epoxidation of ethylene or propylene. Thus, the estimation of a large number of individual rate constants is required for a full PSSA treatment. Furthermore, the previous analysis assumes a low surface coverage of the $C_4H_6O(ads)$ intermediate, and a correspondingly low value for the rate constant k_{-1}. This simplification is probably not valid in the case of a strongly adsorbed $C_4H_6O(ads)$ intermediate, where the activation energy for EpB ring opening has been measured on Ag(110) to be lower than the activation energy for $C_4H_6O(ads)$ ring closure (6). In other words, it is not valid to assume that EpB formation from $C_4H_6O(ads)$ is an irreversible step. Including the rate constant k_{-1} in the previous analysis will result in a decrease in the predicted KIE, possibly bringing it more in line with the values reported in Table 1. Finally, as has been pointed out recently (10), detailed mechanisms derived from macrokinetic data are often misleading. Thus, we instead focus on qualitative aspects of the proposed mechanism in order to demonstrate trends in the experimental results.

With the mechanism in Scheme 1 as a basis for interpreting the data, it is useful to examine the results in Table 1 in closer detail. For example, the $r_{\mathrm{D}}/r_{\mathrm{H}}$ ratio for EpB is seen to be a nearly identical, 1.36–1.38 for C_4D_6 and $CD_2CHCHCD_2$, whereas the rate is practically unchanged for $CH_2CDCDCH_2$. This effect is mirrored by the rate of CO_2 formation, in which a larger decrease in rate is observed for C_4D_6 and $CD_2CHCHCD_2$ than for $CH_2CDCDCH_2$. This observation suggests that rate of further oxidation of the $C_4H_6O(ads)$ intermediate is largely governed by the rate of reaction at its terminal C–H bonds. Oxidation at the 2- and 3-positions apparently has no measurable effect on the rate of combustion.

As shown in Table 1, KIEs have also been detected in the rates of formation of the two minor reaction products, furan and crotonaldehyde. The use of the deuterium-labeled isotopomers results in opposite KIEs for furan and crotonaldehyde formation: the rates of furan formation are increased, whereas the rates of crotonaldehyde formation are decreased. As discussed in the following, this suggests that the rate-determining step for crotonaldehyde formation involves C–H bond cleavage, while the rate-determining step for furan formation does not. The rate of furan formation is observed to increase for all three labeled butadienes, indicating that furan production is also enhanced due to the accumulation of the $C_4H_6O(ads)$ intermediate upon isotopic substitution. Interestingly, the rate increase is greatest for C_4D_6, intermediate for $CH_2CDCDCH_2$, and least for $CD_2CHCHCD_2$. Furan has been shown (2) to be formed from the rapid oxidative dehydrogenation of 2,5-dihydrofuran (2,5-DHF). Because the formation of 2,5-DHF from $C_4H_6O(ads)$ is expected to be the rate-limiting step in furan formation, deuterium substitution at the 1- and 4-positions, by the previous arguments, would increase the rate of formation of furan. However, the rate of furan production will also be controlled by the rate at which furan is consumed by further oxidation to CO_2; the observation that $r_{\mathrm{D}}/r_{\mathrm{H}}$ is higher for $CH_2CDCDCH_2$ than for $CD_2CHCHCD_2$ suggests that the further oxidation of furan at its 3- and 4-positions may have the strongest effect on the net rate of furan formation. The yields of crotonaldehyde, yet another nonselective product, are too low to evaluate trends in reaction rate as a function of the deuterium-labeling position. It is clear, however, that deuterium labeling of butadiene results in a decrease in the rate of formation of crotonaldehyde. Crotonaldehyde is most likely formed via an isomerization of some other C_4H_6O species (EpB, 2,5-DHF, or the strongly adsorbed $C_4H_6O(ads)$ intermediate) that requires hydrogen transfer steps. In isomerization of these species to crotonaldehyde, a 1–4 hydrogen shift involving cleavage of a C–H bond at the 1- or 4-position of butadiene is expected. The observation of a clear KIE for butadiene labeled at the 2- and 3-positions, however, suggests that crotonaldehyde may be formed by a more complex series of steps, and possibly involves hydride transfer steps along the carbon backbone of a C_4H_6O species.

We now briefly consider other mechanistic schemes that could potentially be used to describe the epoxidation of butadiene. For example, one might suggest a scheme in which EpB and CO_2 are produced from parallel channels for the

TABLE 2

Kinetic Isotope Effects in Butadiene Epoxidation on a Cs-Promoted Catalyst

Product	Selectivity[a] (C_4H_6)	TOF, s^{-1} (C_4H_6)	$CH_2CDCDCH_2$ (r_D/r_H)	$CD_2CHCHCD_2$ (r_D/r_H)	$CD_2CDCDCD_2$ (r_D/r_H)	r_D/r_H SD[b]
EpB	96.6%	2.57×10^{-2}	1.01	1.01	0.99	0.02
CO_2	3.4%	9.05×10^{-4}	0.99	0.84	0.85	0.02
Furan	0.0%	0	N/A	N/A	N/A	N/A
Crotonaldehyde	0.0%	0	N/A	N/A	N/A	N/A

[a] Reactor bed temperature = 173°C, butadiene conversion = 8%.

[b] The standard deviation represents the *maximum* standard deviation of the 3 r_D/r_H columns.

reaction of butadiene and oxygen. This pathway is rejected because it cannot account for the significant KIEs observed for EpB formation. In a purely parallel mechanism, a decrease in the rate constant for combustion would lead to an increase in the partial pressure of the reactants, which could in turn lead to an increase in the rate of EpB production. However, at the butadiene conversion levels (1.1%) of our experiments, any decrease in the combustion rate constant would have a negligible effect on the partial pressure of the reactant; i.e., the increase in reactant concentration would be less than 1.1% even if the rate of combustion were *fully* suppressed. This effect is far too small to account for the measured 36% increase in the rate of EpB production. Thus a common surface intermediate is necessary to explain the isotope effects observed.

Nevertheless, it should be pointed out that it is possible to qualitatively explain the observed KIE values for the major products using other mechanistic schemes. For example, a purely sequential scheme is possible, i.e.,

$$C_4H_6 \rightarrow \mathrm{EpB} \leftrightarrow C_4H_6O(\mathrm{ads}) \rightarrow CO_2. \qquad [4]$$

In such a scheme, using D-labeled butadiene would again be expected to lower the rate constant for complete combustion, thus increasing the concentration of the C_4H_6O(ads) intermediate. An increase in the concentration of this surface intermediate would again increase the rate of formation of EpB, consistent with the effects observed in Table 1. We have favored the mechanism of Scheme 1 based on its consistency with the mechanism for ethylene epoxidation previously suggested by Cant and Hall (3). In the case of the less complex ethylene epoxidation reaction, the authors were able to show that this type of model was quantitatively consistent with observed KIEs. Moreover, whether the mechanism suggested in Scheme 1 or Eq. [4] is more representative of the "correct" epoxidation mechanism, the central conclusion of this work is the same: namely, the observed KIE values can be explained by the influence of the strongly adsorbed C_4H_6O(ads) oxametallacycle intermediate on the overall epoxidation kinetics.

Finally, we consider isotope effects for butadiene epoxidation over the Cs-promoted catalyst. In contrast to the unpromoted case, the activity of the promoted catalyst dramatically increased over the first several hours on stream until a high steady-state activity was achieved. This induction period has been attributed to the enhancement of silver dispersion and/or the removal of excess chlorine from the catalyst (11). Due to the greatly improved catalytic activity, a much lower reaction temperature of 173°C was employed. Even at these lower temperatures, the butadiene conversion was nearly 8%, with selectivity to EpB greater than 96%. Carbon dioxide was the only nonselective product detected. Table 2 summarizes the observed KIE data for the promoted catalyst. No effect on the rate of EpB formation is discernible for any of the isotopically labeled butadienes, but a small decrease in the rate of CO_2 formation is observed. These results are consistent with the basic mechanism shown in Scheme 1; because the rate of EpB formation is so much greater than the rate of CO_2 formation, small changes in the rate constants for combustion will have no measurable effect on the rate at which EpB is produced. It has been suggested that the role of the Cs promoter is to increase the rate of EpB formation from the strongly adsorbed C_4H_6O intermediate (2, 6) by lowering the desorption energy of strongly bound EpB. That is, in terms of the mechanism of Scheme 1, the addition of Cs results in a substantial increase in k_1. The observed KIE values for CO_2 again suggest that combustion is initiated by C–H bond cleavage at the 1- and 4-positions of butadiene. In summary, these studies indicate that there are apparent similarities between the mechanisms of the silver-catalyzed epoxidation of ethylene and butadiene, as evidenced by similar trends in KIE values for unpromoted catalysts. However, key differences in the product distribution complexity, adsorption energy of the products, and promoter levels used in industrial catalysts point to opportunities for elucidating the mechanism of olefin epoxidation through comparative studies of these chemistries.

CONCLUSIONS

Selectively deuterated 1,3-butadiene isotopomers have been used to study KIEs in the silver-catalyzed epoxidation of butadiene. On unpromoted silver catalysts, epoxybutene formation is characterized by an inverse KIE that results from a primary effect in total oxidation to CO_2. These KIEs are only significant for butadiene isotopomers that are D-labeled in the 1- and 4-positions, indicating that combustion is initiated by cleavage of a terminal C–H bond. In analogous fashion to previous KIE studies for the epoxidation of ethylene, the observed KIEs can be explained by a reaction scheme in which both partial and total oxidation products are generated from a common C_4H_6O(ads) surface intermediate. This scheme is also consistent with previous surface science experiments, suggesting that the C_4H_6O(ads) intermediate may be a surface oxametallacycle. The results of KIE experiments conducted over Cs-promoted silver catalysts are also in accord with the proposed reaction scheme and demonstrate that the function of the Cs promoter may be to lower the activation energy for epoxybutene formation from the C_4H_6O(ads) species.

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