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Isotope effect and selectivity promotion in ethylene oxidation on silver

C. Stegelmann, P. Stoltze [*]

Aalborg University, Niels Bohrs Vej 8 DK-6700 Esbjerg, Denmark

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Abstract

The kinetic isotope effect and the selectivity promotion of ethylene epoxidation were investigated with the recently published microkinetic model (C. Stegelmann et al., J. Catal. 221 (2004) 630). Results calculated from the model for the previously published parameters are in good agreement with experimental data.

Keywords: Ethylene; Epoxidation; Microkinetic model; Promotion; Silver

Recently we published a microkinetic model based on surface science explaining the steady-state kinetics of ethylene epoxidation, ethylene combustion, and ethylene oxide combustion for a wide range of reaction conditions on unpromoted silver [1]. In addition, the model explains a broad range of transient surface science experiments [2,3]. The main idea of the model [1] is that a surface oxide (nucleophilic oxygen) is formed upon which ethylene and atomic oxygen (electrophilic oxygen) adsorb competitively. The adsorbed ethylene and electrophilic oxygen react to form an oxametallacycle, which branches into ethylene oxide and acetaldehyde. In the presence of oxygen, acetaldehyde rapidly combusts to CO_2. Ethylene oxide may isomerize to acetaldehyde through the oxametallacycle and combust to CO_2. The oxametallacycle is therefore a common intermediate for ethylene epoxidation, ethylene combustion, and ethylene oxide combustion. Ethylene also combusts through a parallel pathway, presumably through a vinyl alcohol intermediate. The key idea of the microkinetic model [1] is that epoxidation and combustion go through a common intermediate (oxametallacycle), as suggested by Campbell et al. [4,5] and Barteau et al. [6,7].

Medlin et al. [13] have found that in the epoxidation of 1,3-butadiene to 3,4-epoxy-butene over silver, the epoxidation and the total oxidation proceed through a common intermediate. The epoxidations of ethylene and butadiene are closely related reactions, the main difference being that 3,4-epoxy-butene is much more strongly adsorbed on silver than is ethyleneoxide.

Implicit in the model are an obvious opportunity for a simple explanation of the inverse isotope effect [8–10] and of selectivity promotion. In this letter we investigate these two explanations by the same mechanism, thermodynamic and kinetic parameters, as used in the simulation of steady-state kinetics in previous work [1].

The simple explanations we use here are obvious, and agreement between the model and experiments will not rule out alternative or more detailed explanations. However, disagreement would present a serious problem for the microkinetic model and challenge the current understanding of the reaction mechanism. Fortunately, we find that the model is in good agreement with experiments.

The substitution of deuterium for hydrogen in ethylene results in a huge isotope effect [8–10]. The formation of CO_2 decreases by a normal isotope effect; however, the formation of ethylene oxide increases by a large inverse isotope effect, resulting in a significant increase in selectivity [8–10]. Isotope effects are usually large when ordinary hydrogen (H) is replaced by deuterium (D). Under most circumstances the predominant factor in an isotope effect is the zero-point energy (ZPE): when an atom is replaced by a dif-

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[*] Corresponding author. Fax: +45 75 45 36 43.
E-mail address: stoltze@aaue.dk (P. Stoltze).

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ferent isotope of the same element, there is no change in the electronic ground-state energy, but there are changes in vibrational frequencies (ν) and therefore in zero-point energies ($\frac{1}{2}h\nu$). It has therefore been concluded that the breaking of C–H bonds must be rate limiting in ethylene combustion (Ref. [8,11] and references therein). An analysis of hydrogen transfer processes shows that the ratio k_H/k_D is determined almost entirely by ZPE differences in the initial state [12]. The initial ZPE difference varies slightly for different molecular H-transfer systems and is usually in the range of 3–5.5 kJ/mol [12].

In Fig. 1 the experiments of Cant and Hall [9] are simulated by the microkinetic model, with the assumption that the barrier of elementary steps involving C–H bond breaking increases by 4.5 kJ/mol in the case where deuterated ethylene is applied.

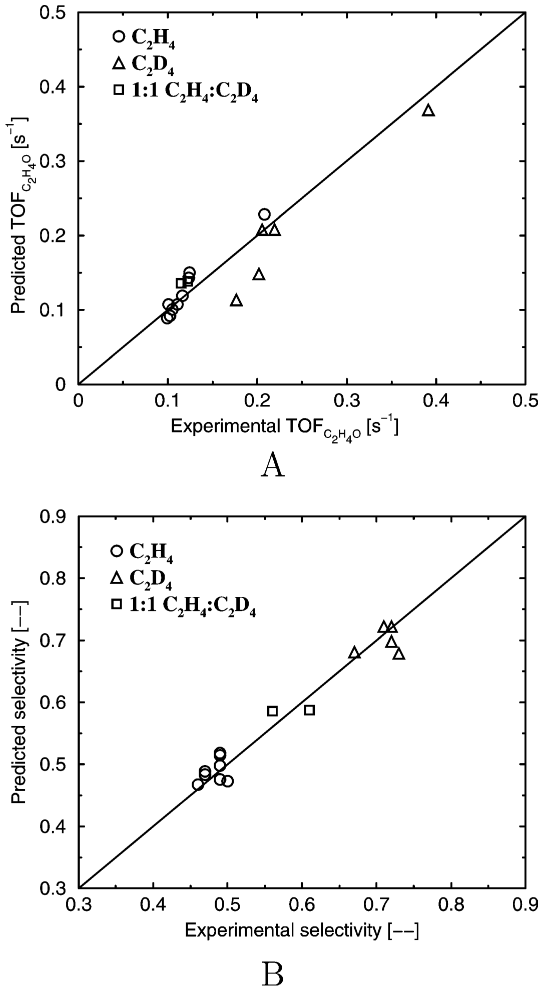

Fig. 1. Experimental versus predicted results for kinetic experiments with and without deuteriated ethylene. (A) is the activity for ethylene oxide formation, (B) is the selectivity. The experiments were conducted at 418–438 K, $P_{O_2} = 8.6$ kPa, and $P_{C_2H_4} = 0.8$–1.6 kPa in a differential reactor [9]. The kinetic model used in the calculations includes the epoxidation of ethylene and the oxidations of ethylene and of ethyleneoxide. Mechanistic details and all parameters have been published in [1].

It is apparent from Fig. 1 that the microkinetic model explains the isotope effect almost quantitatively. This can be explained by the fact that the formation of oxametallacycle that is, the common intermediate to epoxidation and combustion, does not require C–H bond breaking, and the formation rate of oxametallacycle is not directly influenced by the use of deuterated ethylene. However, the branching of the oxametallacycle into combustion products (acetaldehyde) requires C–H bond breaking, and the formation rate of acetaldehyde decreases for deuterated ethylene. As the formation rate of acetaldehyde decreases, the formation rate of ethylene oxide has to increase as the formation rate of oxametallacycle is unchanged, which leads to increased selectivity for deuterated ethylene.

A similar analysis based on DFT was performed by Linic and Barteau [7], leading to the same conclusions as in this work. As Linic and Barteau have pointed out [7], the large inverse isotope effect for selectivity highlights the importance of the branching ratio of the oxametallacycle.

From the above findings for isotope effects it is natural to suggest that selectivity promoters such as alkali and chlorine work by modifying the branching ratio of the oxametallacycle. It is likely that chlorine and alkali will influence the stabilities of the transition states between the oxametallacycle and ethylene oxide (TST1) and between the oxametallacycle and acetaldehyde (TST2), respectively. The difference in activation barriers for ethylene oxide and acetaldehyde (ΔH^{TST})

$$\Delta H^{\mathrm{TST}} = H^{\ddagger}_{\mathrm{CH_3CHO}} - H^{\ddagger}_{\mathrm{C_2H_4O}}, \qquad (1)$$

where $H^{\ddagger}_{\mathrm{C_2H_4O}}$ and $H^{\ddagger}_{\mathrm{CH_3CHO}}$ are the activation barriers for ethylene oxide and acetaldehyde formation, respectively, from the oxametallacycle. The selectivity calculated from the microkinetic model is shown at two different temperatures close to industrial reaction conditions in Fig. 2. It is

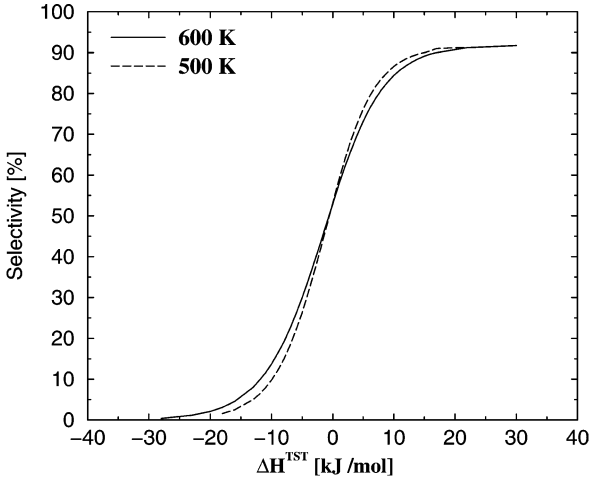

Fig. 2. Calculated selectivity versus the enthalpy difference between the transition states for ethylene oxide and acetaldehyde formation, respectively, at different temperatures. $P_{O_2} = P_{C_2H_4} = 100$ kPa.

clear that the selectivity increases significantly with increasing ΔH^{TST}. The value $\Delta H^{\mathrm{TST}} = 0.0$ kJ/mol corresponds to the unpromoted microkinetic model. When ΔH^{TST} is varied slightly from the value 0.0 kJ/mol, the selectivity rapidly increases or decreases, that is, relatively small shifts in the stability of the transition states may influence the selectivity significantly. However, far from 0.0 kJ/mol changes in ΔH^{TST} lead only to moderate variations in selectivity. The selectivity approaches zero for large negative values of ΔH^{TST}, but saturates below 100% (90%) for large positive values. The saturation selectivity of 90% corresponds very well to the maximum selectivities reported in the literature (Ref. [11] and references therein). The selectivity does not reach 100% because the direct combustion of ethylene is included in the kinetic model [1].

It is observed from the figure that the temperature has an insignificant influence on the relation between selectivity and ΔH^{TST}.

Recently Linic and Barteau [14] showed by DFT that Cs can enhance selectivity for ethylene oxide by stabilizing the transition state for formation of ethylene oxide with respect to the transition state to acetaldehyde.

It may seem surprising that both electropositive alkalis and electronegative chlorine promote selectivity. However, chlorine is known to diffuse to subsurface positions at the temperatures of epoxidation [15–17]. The electronic effect of subsurface electronegative chlorine on the transition states TST1 and TST2 may therefore be similar to that of alkali positioned on the surface. However, this remains to be demonstrated by DFT or experiment.

To conclude, it has been demonstrated that our previously developed microkinetic model for unpromoted silver may explain isotope effects and selectivity promotion. The key step of the microkinetic model explaining these features is the formation of a common intermediate, which may branch into either ethylene oxide or combustion products.

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References

[1] C. Stegelmann, N.C. Schiødt, C.T. Campbell, P. Stoltze, J. Catal. 221 (2004) 630–649.
[2] C. Stegelmann, P. Stoltze, J. Catal. 226 (2004) 129–137.
[3] C. Stegelmann, P. Stoltze, Surf. Sci. 552 (2004) 260–272.
[4] C.T. Campbell, J. Catal. 94 (1985) 436–444.
[5] C.T. Campbell, J. Catal. 99 (1986) 28–38.
[6] S. Linic, M.A. Barteau, J. Catal. (2003) 200–212.
[7] S. Linic, M.A. Barteau, J. Am. Chem. Soc. 125 (2003) 4034–4035.
[8] R.B. Grant, R.M. Lambert, J. Catal. 92 (1985) 364–375.
[9] N.W. Cant, W.K. Hall, J. Catal. 52 (1978) 81–94.
[10] R.A. van Santen, J. Moolhuysen, W.M.H. Sachtler, J. Catal. 65 (1980) 478–480.
[11] R.A. van Santen, H.P.C.E. Kuipers, Adv. Catal. 35 (1987) 265–321.
[12] K.J. Laidler, Chemical Kinetics, third ed., HarperCollins, New York, 1987, chap. 11.
[13] J.W. Medlin, J.R. Monnier, M. Barteau, J. Catal. 204 (2001) 71–76.
[14] S. Linic, M.A. Barteau, J. Am. Chem. Soc. 126 (2004) 8086–8087.
[15] H. Piao, K. Adib, M.A. Barteau, Surf. Sci. 557 (2004) 13–20.
[16] J.R. Monnier, J.L. Stavinoha Jr., G.W. Hartley, J. Catal. 226 (2004) 321–333.
[17] J.R. Monnier, J.L. Stavinoha Jr., R.L. Minga, J. Catal. 226 (2004) 401–409.