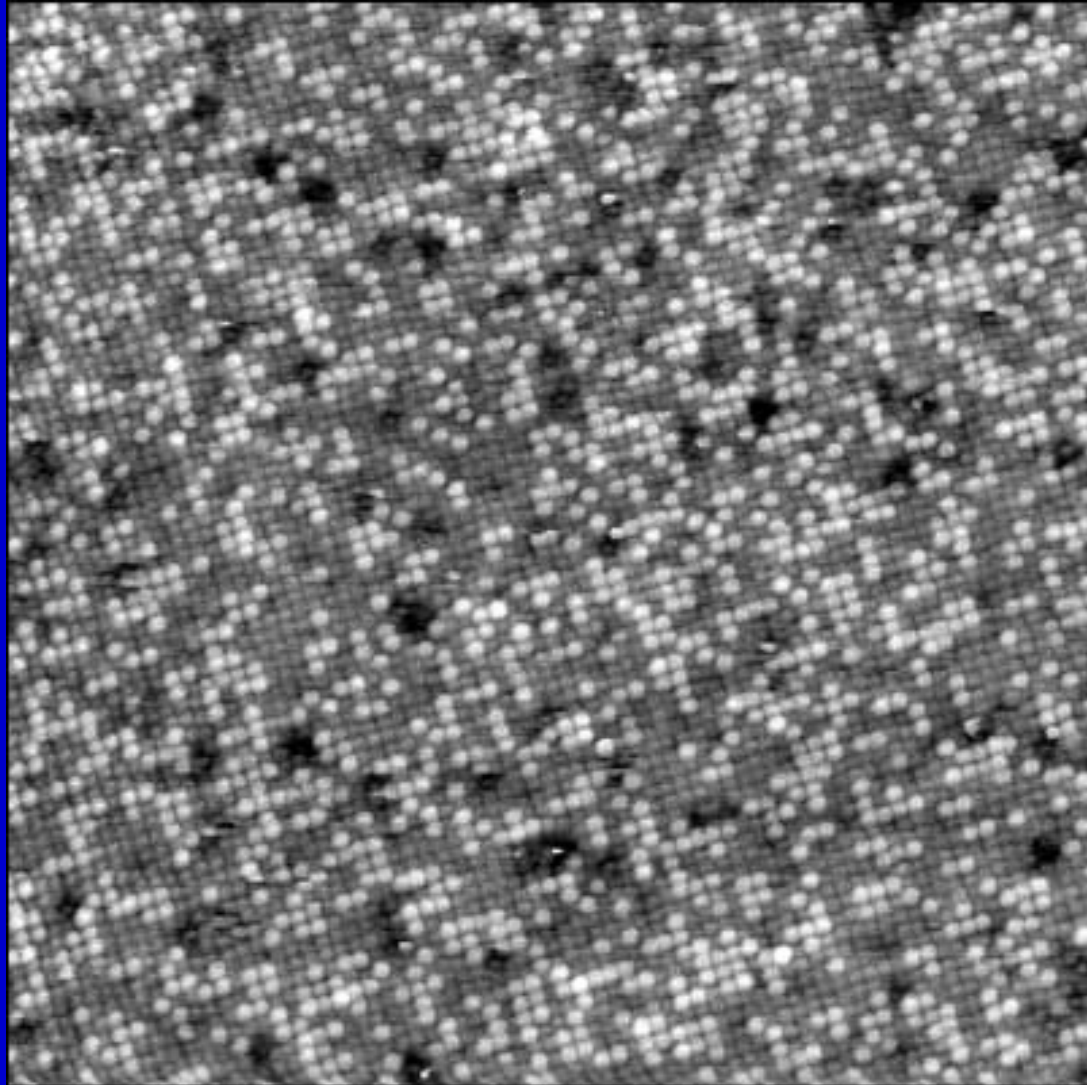


# Chemical reactions on solid surfaces play critical roles in many technologies:



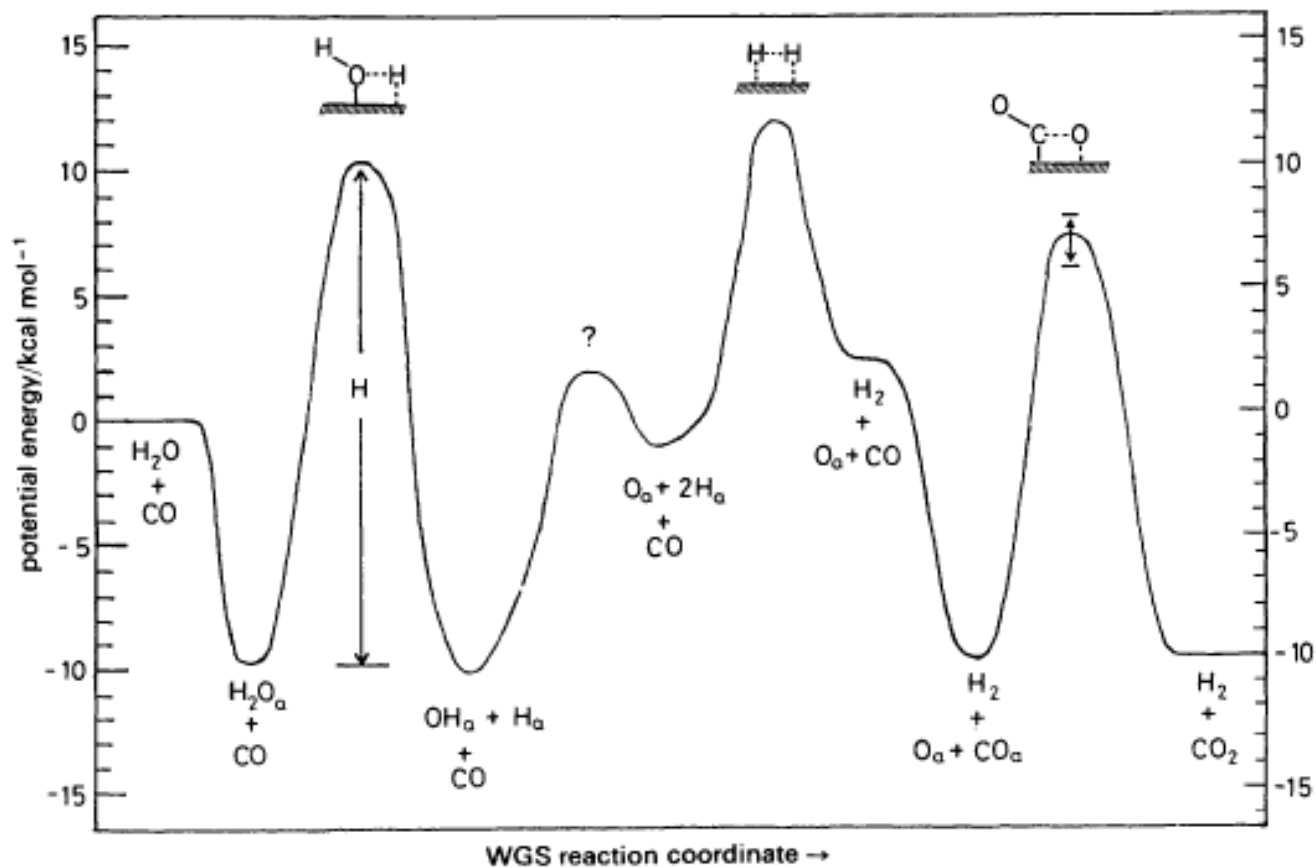
Institut für Allgemeine Physik, TU Wien

Atomic-resolution STM image of alloy surface from group of Peter Varga, TU Vienna

1. Catalysts for producing fuels, pollutant removal and chemical production
2. Microelectronics fabrication
3. Electro optic devices
4. Solar energy devices
5. Nanotechnology
6. Chemical / biochemical sensors

**Part 2: A very short summary of some  
important considerations in the  
kinetics of  
surface-catalyzed reactions**

# Elementary step energy diagram: Water-gas shift on Cu(110)



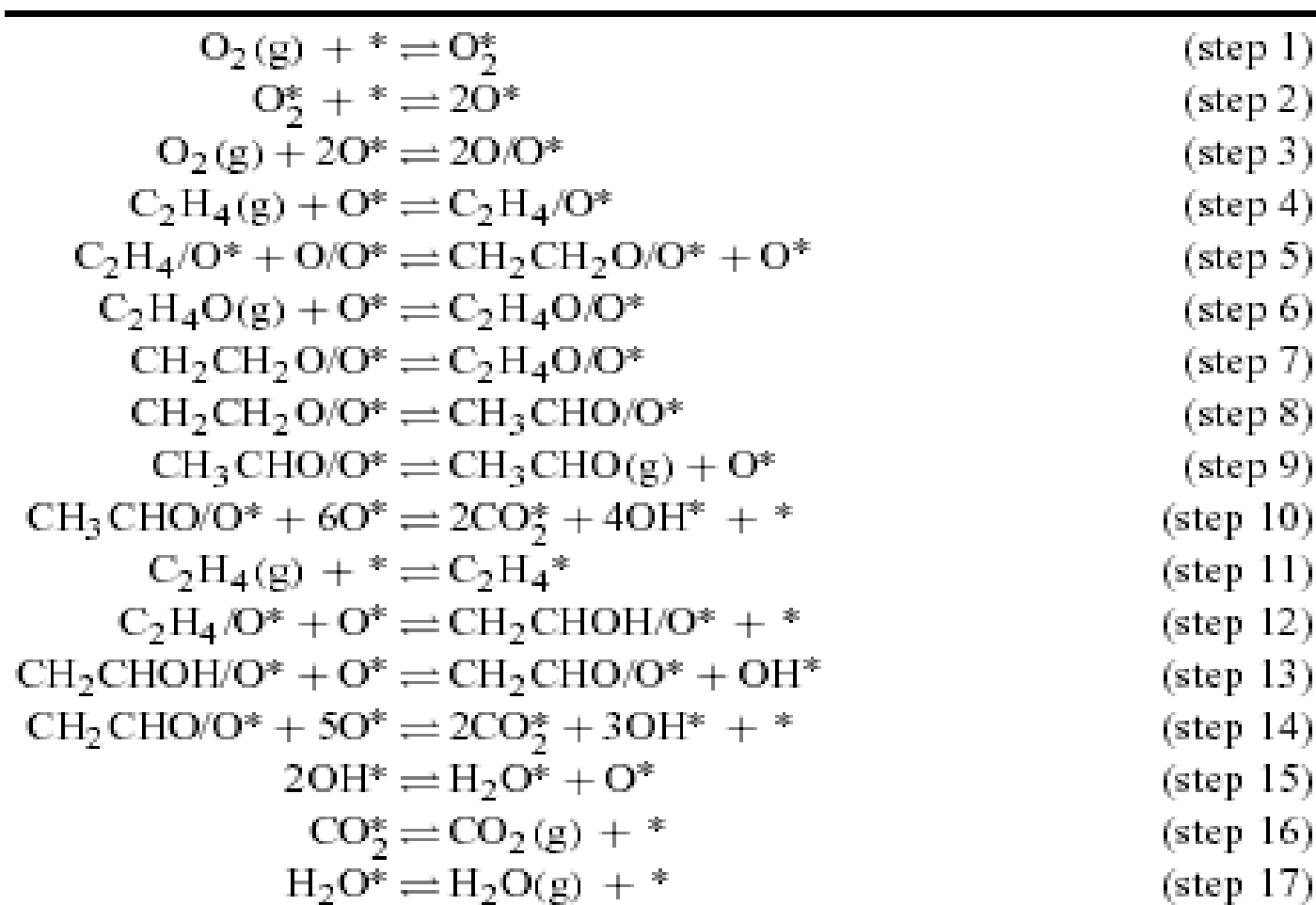
J. Nakamura and CTC, Faraday Trans. 86 (1990) 2725

# Microkinetic modeling of ethylene oxidation over silver

C. Stegelmann, N.C. Schiødt, C.T. Campbell and P. Stoltze, J. Catal. 221 (2004) 630.

Table 1

Reaction mechanism for the microkinetic model (modified Barteau mechanism)



The asterisk signifies a metallic silver site,  $/O^*$  is a surface oxide site, and  $X^*$  and  $Y/O^*$  are an adsorbed species on metallic silver and surface oxide, respectively.

# “The Degree of Rate Control”

Mathematical construct for quantifying which steps in mechanism are kinetic bottlenecks, or rate-controlling

First introduced: CT Campbell, Topics in Catalysis 1 (1994) 353.

Best explanation: CT Campbell, J. Catal. 204 (2001) 520.

The degree of rate control for elementary step i :

$$X_{rc,i} = \left( \frac{\delta R}{\delta k_i} \right)_{K_j, K_{j \neq i}} \cdot (k_i / R),$$

where R = net rate to desired product,

$k_i$  = rate constant for step i

$K_i$  = eqbm constant for step i

Tells how much the net rate increases per unit increase in rate constant for step i (both on a % basis)

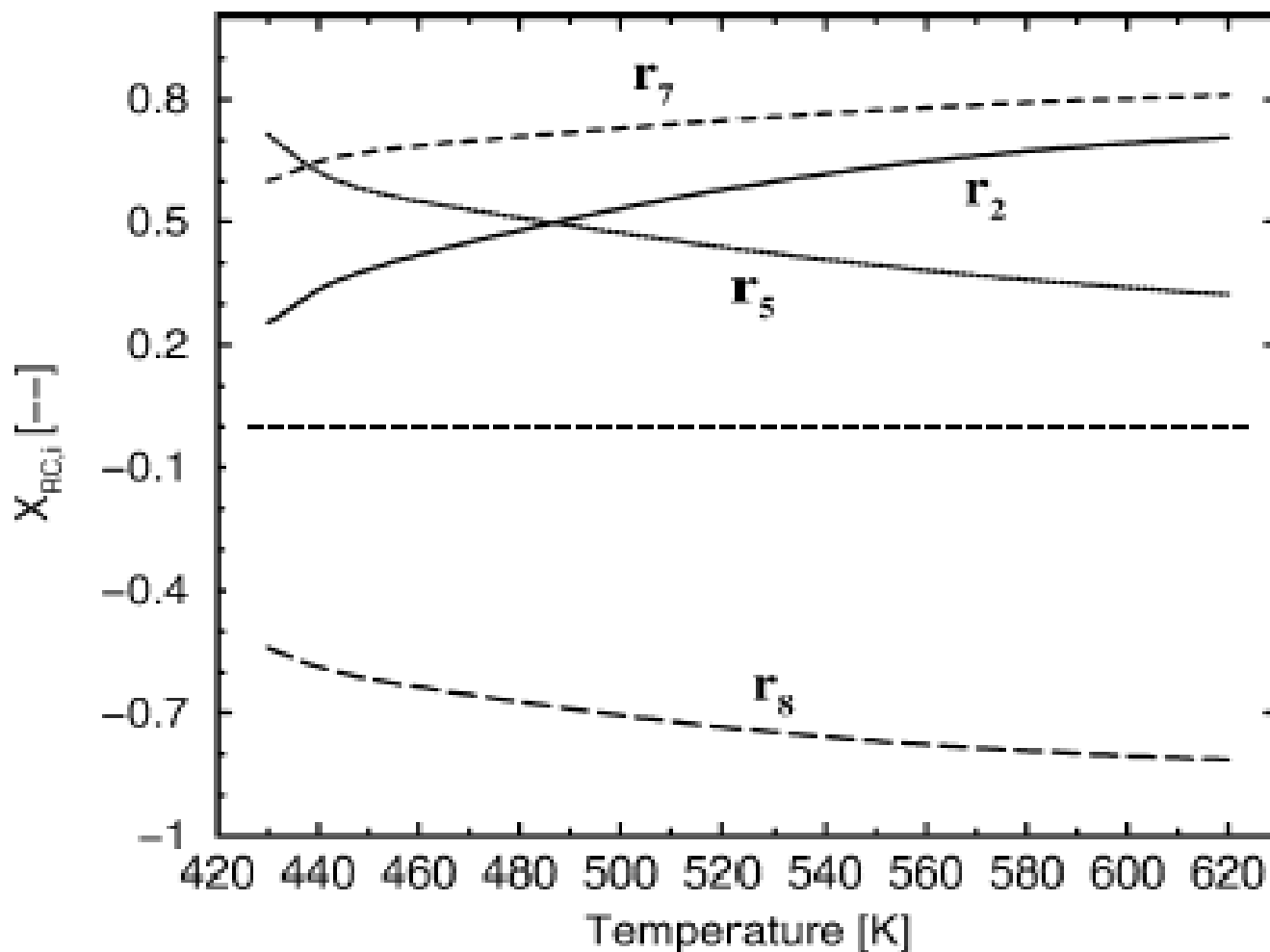
If there is a single rate-determining step (RDS),

$$X_{rc,RDS} = 1$$

Note that:

$$\sum_i X_{rc,i} = 1$$

## Degree of rate control for key steps versus temperature: Selective ethylene epoxidation over Ag



Only shown for  
“kinetically relevant”  
steps.

For other 13 steps:

←  $X_{RC,i} = \sim 0$

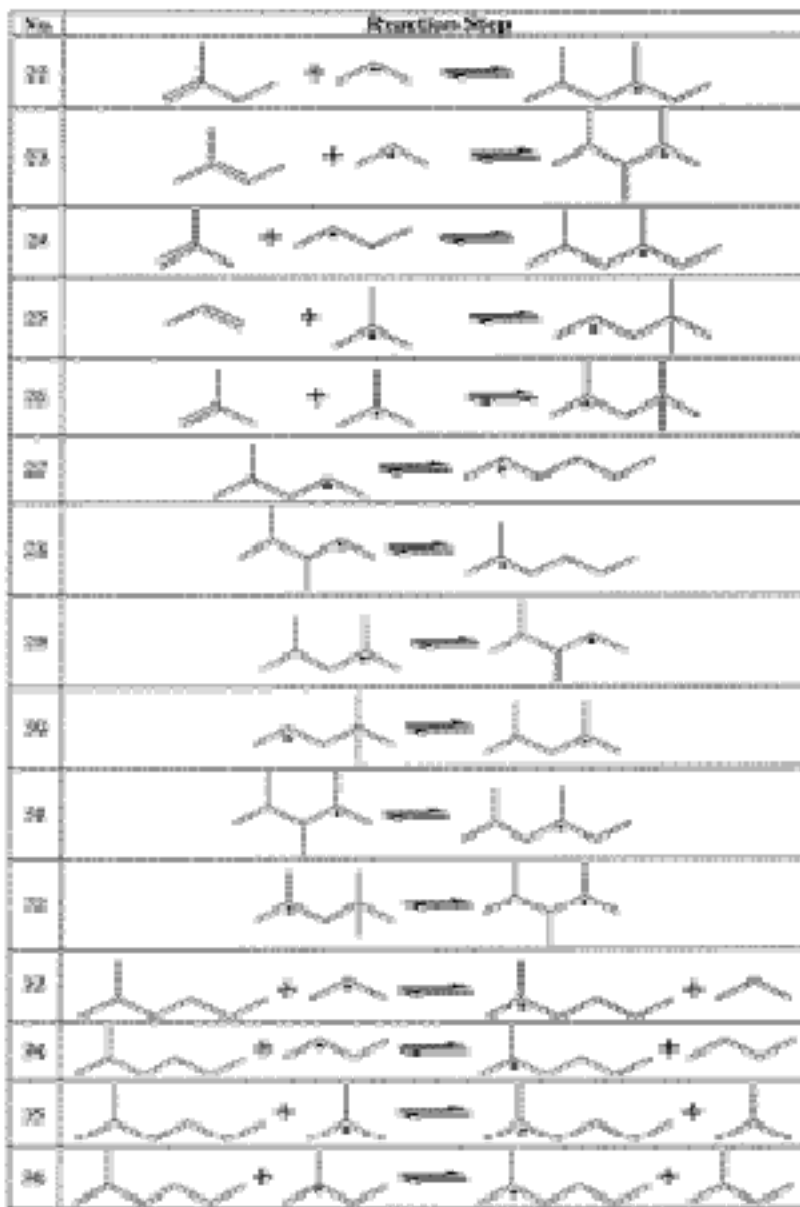
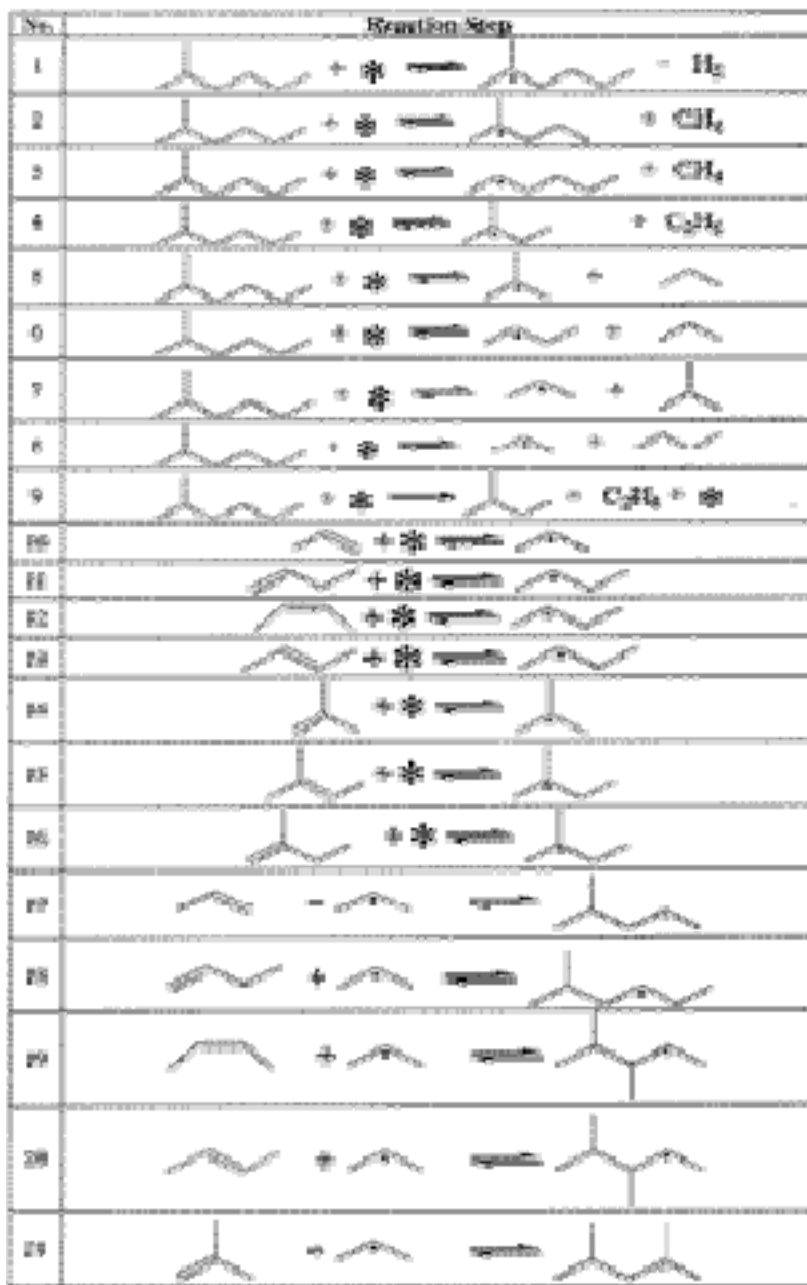
Fig. 8. Degree of rate control for ethylene oxide formation versus temperature at industrial reaction conditions.  $P_{O_2} = P_{C_2H_4} = 100$  kPa.

*C. Stegelmann et al. / Journal of Catalysis 221 (2004) 630–649*

Degree of rate control reported in microkinetic model for same reaction by Linic and Barteau, *J. Catal.* 214 (2003) 200.

## Simplified reaction scheme for 2-methylhexane conversion over USY zeolite.

N Agarval, MA Sanchez-Castillo, RD Cortright, [RJ Madon](#) & [JA Dumesic](#), Ind. Engr. Chem. Res. 41 (2002) 4016.



Reaction Steps with the Highest Degree of Rate Control ( $X_{RC,i}$ )  
for ~30% Conversion of 2-Methylhexane at 773 K

Step	$X_{RC,i}$
	0.47
	0.18
	0.15
	0.12
	0.09
	0.06
	0.05
	0.05
	0.03
	0.03
	-0.03
	-0.08
	0.02



Only 5 steps have  
bigger than 6%  
effect!!

<sup>a</sup> The feed consists of 10 mol % 2-methylhexane and no olefins.

Their later study of  
a rxn w/ 370 steps  
showed only ~10 were  
kinetically significant:  
J. Catal. 205 (2002) 67

# TIAX has incorporated Degree of Rate Control calculations in Bistro™, their software for implementing microkinetics of reaction mechanisms.

Calculate transient performance of chemical reactor using MATLAB.

Export models to Runway™ (system simulator)

Specify time dependent or constant inlet conditions

Control solution of the stiff differential equations.

- Thermo-physical properties
- Adiabatic
  - CSTR, PFR, Film PFR
- TPD and TPR
  - CSTR, PFR
  - Sensitivity analysis

- Easy entry of reactions and parameters
- Re-use of previously validated parameters

Elementary reactions	A <sub>f</sub>	E <sub>f</sub>	A <sub>b</sub>	ΔH	α	σ	ΔΔH	ΔΔS
Pt + N2 = N2Pt	1.00e+3	0.0	1.00e+11	-60.0	0.5	-1	-19.9	-80.3
NO + Pt = NOPt	1.00e+3	0.0	1.00e+9	-90.0	0.5		53.9	19.9
NOPt + Pt = NPt + OPt	5.00e+13	70.0	3.00e+15	-146.5	0.5		-72.3	-260.8
N2Pt + Pt = 2 NPt	3.40e+10	130.0	1.00e+12	-25.0	0.5	1	-20.4	-41.8
NOPt + NPt = N2Pt + OPt	1.00e+13	100.0	2.00e+11	-122.0	0.5	2	210.0	-55.4
O2 + 2 Pt = O2Pt2	4.00e+3	0.0	1.00e+9	-37.6	0.5	-2		
O2Pt2 = 2 OPt	5.42e+12	4.1	8.00e+15	-170.0	0.5	-2		
NOPt + OPt = NO2Pt2	1.00e+9	120.0	2.00e+11	-120.0	0.5			
NO2 + 2 Pt = NO2Pt2	1.00e+3	0.0	1.00e+9	-70.0	0.5	2		
2 NO + O2 + BaO2 = BaN2O6	1.00e+0	60.0	1.00e+17	-140.0	0.5			
N2O6 + 4 Pt = BaO2 + 2 NOPt + 2 OPt	1.00e+10	120.0	1.00e+17	-210.0	0.5	1		
NO + OPt = BaO2 + Pt	1.00e+10	60.0	1.00e+8	-37.6	0.5			
N2O6 + 4 Pt = BaO2 + 2 NO2Pt2	1.00e+7	100.0	1.00e+15	-100.0	0.5	-1		

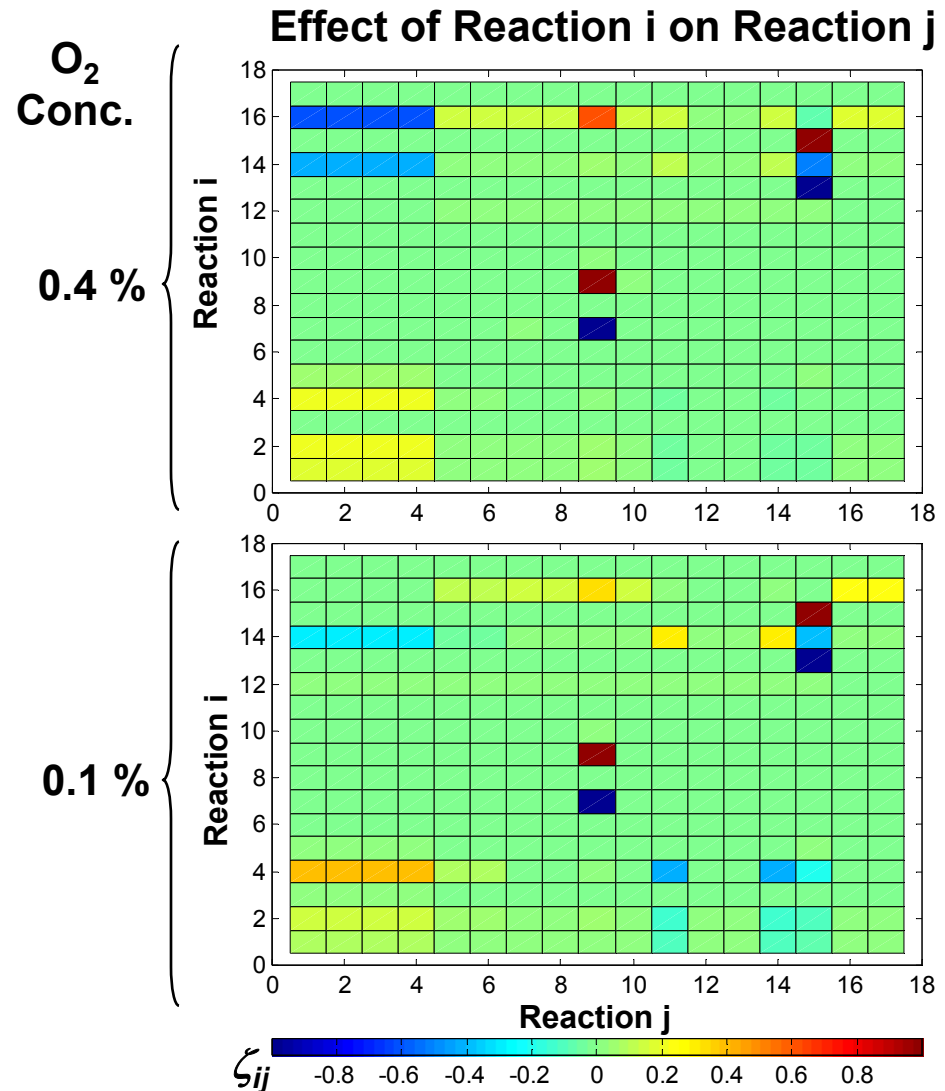
at T= 700.0 K



For example, in ammonia formation in 3-way catalytic converters, TIAX found N<sub>2</sub> and O<sub>2</sub> adsorption to be kinetically significant only at high coverage.

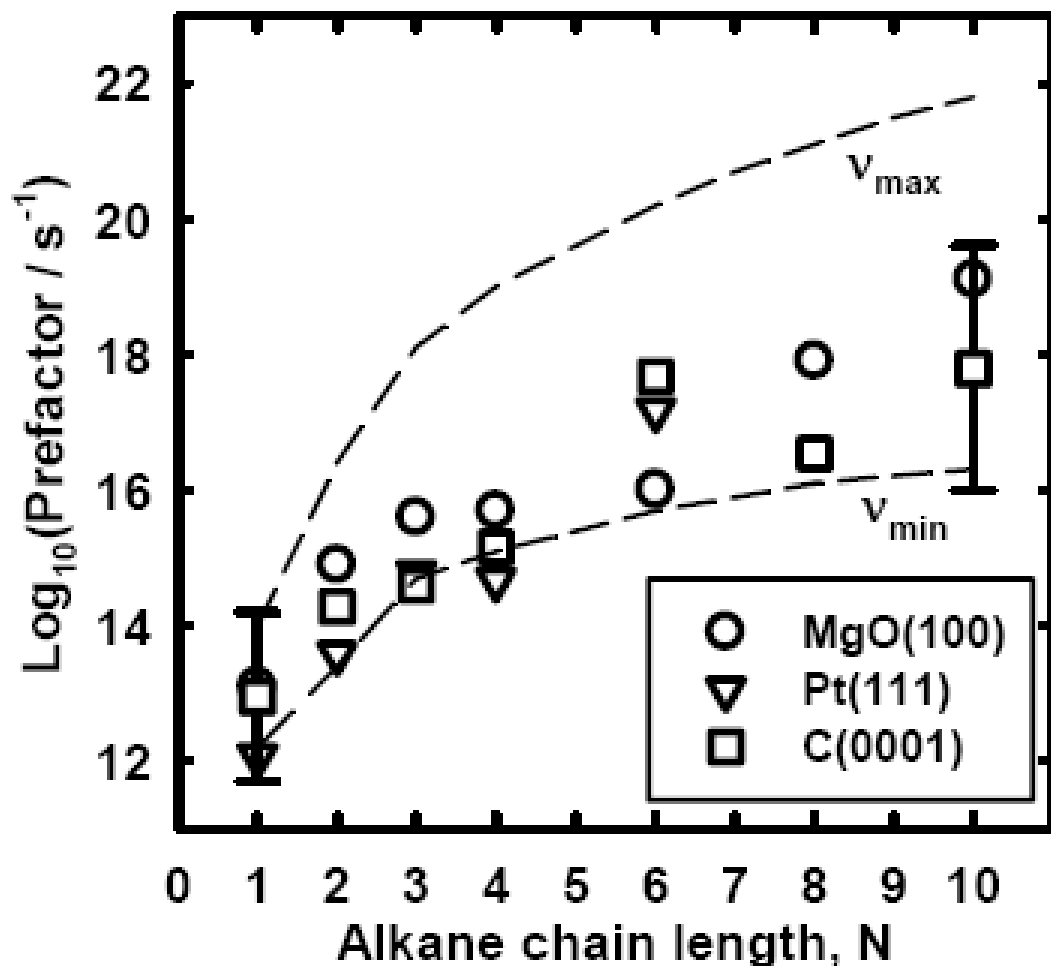
### Reaction Network

- 1  $\text{NH}_3 + \text{Rh} = \text{NH}_3\text{Rh}$
- 2  $\text{NH}_3\text{Rh} + \text{Rh} = \text{NH}_2\text{Rh} + \text{HRh}$
- 3  $\text{NH}_2\text{Rh} + \text{Rh} = \text{NHRh} + \text{HRh}$
- 4  $\text{NHRh} + \text{Rh} = \text{NRh} + \text{HRh}$
- 5  $\text{H}_2 + \text{Rh} = \text{H}_2\text{Rh}$
- 6  $\text{H}_2\text{Rh} + \text{Rh} = 2 \text{HRh}$
- 7  $\text{HRh} + \text{ORh} = \text{OHRh} + \text{Rh}$
- 8  $\text{H}_2\text{O} + \text{Rh} = \text{H}_2\text{ORh}$
- 9  $\text{H}_2\text{ORh} + \text{ORh} = 2 \text{OHRh}$
- 10  $\text{HRh} + \text{OHRh} = \text{H}_2\text{ORh} + \text{Rh}$
- 11  $\text{Rh} + \text{N}_2 = \text{N}_2\text{Rh}$
- 12  $\text{NO} + \text{Rh} = \text{NORh}$
- 13  $\text{NORh} + \text{Rh} = \text{NRh} + \text{ORh}$
- 14  $\text{N}_2\text{Rh} + \text{Rh} = 2 \text{NRh}$
- 15  $\text{NORh} + \text{NRh} = \text{N}_2\text{Rh} + \text{ORh}$
- 16  $\text{O}_2 + 2 \text{Rh} = \text{O}_2\text{Rh}_2$
- 17  $\text{O}_2\text{Rh}_2 = 2 \text{ORh}$



# Prefactors for Desorption Rate Constant for Linear Alkanes on MgO(100), Pt(111) and C(0001)

Steven L. Tait, Zdenek Dohnálek, CTC, Bruce D. Kay  
J. Chem. Phys. **122**, 164708 2005; and **125**, 234308 2006.



$$v_{TST} = \left( \frac{k_B T}{h} \right) \frac{q^\ddagger}{q_{ads}}$$

Adsorbate more localized than transition state ( $\ddagger$ ): larger  $q$ .

Adsorbates at step edges:  
EVEN BIGGER prefactors!

DE Starr and CTC,  
Pb desorption from Mo(100)  
(in preparation)

# Prefactors for dissociation of adsorbates $\sim 10^{10} - 10^{12} \text{ s}^{-1}$ (transition state more localized than adsorbed reactant)

Table 1  
Preexponential factors for the dehydrogenation of adsorbed hydrocarbon species

System	$k_r^{(0)}/k_d^{(0)}$	$\nu_{\text{diss}} / \text{S}^{-1}$	$E_r$ (kcal/mol)	Ref.
$\text{C}_2\text{H}_6$ on Pt(111)	$8 \times 10^{-4}$	$8 \times 10^9 \text{ a)}$	16.4	
$\text{C}_2\text{H}_4$ on Pt(111)		$4 \times 10^{10}$	14.9	
di- $\sigma$ -c- $\text{C}_5\text{H}_8$ on Pt(111)	$1 \times 10^{-2}$	$10^{11} \text{ a)}$	13.3	
di- $\sigma$ -c- $\text{C}_6\text{H}_{10}$ on Pt(111)	$6 \times 10^{-2}$	$6 \times 10^{11} \text{ a)}$	14.3	
c- $\text{C}_6\text{H}_{12}$ on Pt(111)	$3 \times 10^{-1}$	$3 \times 10^{12} \text{ a)}$	13.2	
$\text{CH}_3\text{CH}_2\text{C}-$ on Pt(111)		$4 \times 10^{11}$	22.5	
$\text{CH}_3\text{C}-$ on Pt(111)		$6 \times 10^{11}$	27	
n- $\text{C}_4\text{H}_{10}$ on Pt(110)-(1 $\times$ 2)	$5 \times 10^{-3}$	$5 \times 10^{10} \text{ a)}$	11.5	
$\text{C}_3\text{H}_8$ on Pt(110)-(1 $\times$ 2)	$7 \times 10^{-3}$	$7 \times 10^{10} \text{ a)}$	10.8	
$\text{C}_2\text{H}_6$ on Pt(110)-(1 $\times$ 2)	$5 \times 10^{-3}$	$5 \times 10^{10} \text{ a)}$	10.3	
$\text{CH}_4$ on Pt(110)-(1 $\times$ 2)	$6 \times 10^{-1}$	$6 \times 10^{12} \text{ a)}$	18.4	
$\text{C}_2\text{H}_6$ on Ir(110)-(1 $\times$ 2)	$3 \times 10^{-3}$	$3 \times 10^{10} \text{ a)}$	5.5	
$\text{C}_2\text{H}_2$ on Ni(111)		$1 \times 10^{14}$	28	
$\text{CH}_4$ on Rh film	$2 \times 10^{-3}$	$2 \times 10^{10} \text{ a)}$	11.0	
$\text{Cp}^*\text{Rh}(\text{CO})(\text{C}_6\text{H}_{12}) \rightarrow$ $\text{Cp}^*\text{Rh}(\text{CO})(\text{C}_6\text{H}_{11})(\text{H})$		$10^{11}$	4.8	

a) Assumed that  $k_d^{(0)} = 10^{13} \text{ s}^{-1}$  to calculate  $k_r^{(0)}$  from measured ratio  $k_r^{(0)}/k_d^{(0)}$ .

# Prefactors for Pd<sub>n</sub> cluster migration on MgO(100) (now from DFT calculations) **INCREASE WITH CLUSTER SIZE!**

Lijun Xu, Graeme Henkelman, CTC, and Hannes Jonsson,  
Surf. Sci. 600, 1351 (2006).

Event	Barrier (eV)	Prefactor (s <sup>-1</sup> ) <sup>†</sup>	
1(a) monomer hop, terrace	0.34	7.35 × 10 <sup>11</sup>	← monomer hop
2(a) dimer hop (a), terrace	0.43	4.16 × 10 <sup>10</sup>	
2(b) dimer hop (b), terrace	0.11	2.01 × 10 <sup>12</sup>	← Pd <sub>2</sub> hop
2(c) dimer slide, terrace	0.60	3.59 × 10 <sup>10</sup>	
2(d) dimer hop/dissociation, terrace	0.56	3.0 × 10 <sup>14</sup>	
2(e) dimer dissociation, terrace	0.84	4.14 × 10 <sup>11</sup>	
2(f) dimer dissociation, F-center	0.88		
2(g) dimer dissociation, F-center	0.70		
2(h) dimer contraction, F-center	0.11		
3(a) trimer hop (a), terrace	0.48	5.37 × 10 <sup>10</sup>	
3(b) trimer hop (b), terrace	0.21	4.36 × 10 <sup>12</sup>	← Pd <sub>3</sub> hop
3(c) trimer slide, terrace	0.94	3.38 × 10 <sup>11</sup>	
3(d) trimer dissociation, terrace	1.38 <sup>‡</sup>		
3(e) trimer dissociation, F-center (1)	1.23 <sup>‡</sup>		
3(f) trimer dissociation, F-center (2)	1.09 <sup>‡</sup>		
4(a) tetramer hop, terrace	0.41	1.28 × 10 <sup>14</sup>	← Pd <sub>4</sub> hop: ← 200x larger than monomer!

# Acknowledgements

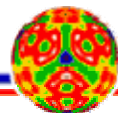
**Todd Stuckless, Dave Starr, Jeff Raney, Jane Larsen, Michael Gottfried, P. Bera, Hyeran Ihm, Henry Ajo, Steve Parker, Steven Diaz, Noah Shamir, Maria Smedh, Dan Bald, Jonathan Harris, Ole Lytken, Wanda Lew, Jason Farmer, Nancy Ruzycki, Jack Baricuatro; Pat Stayton, Rikki and Gil Goobes; Gibum Kim, Hann Wen Guan, Tim Londergan J. Chevallier (Aarhus Univ.), H. Coufal (IBM Almaden), DA King (UK)**



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