

Carbon–Carbon Bond Cleavage and Dehydrogenation of Isobutane Over HZSM-5 at Low Pressures and Temperatures

Cam Le Minh · Abdullah K. Alanazi ·
David J. Miron · Trevor C. Brown

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Abstract Carbon–carbon bond cleavage and dehydrogenation are observed following low-pressure activation of isobutane over HZSM-5. Temperature-dependent rate parameters were determined by flexible least squares modelling of the propene and isobutene formation data. Apparent activation energies are $73.9 \pm 2.4 \text{ kJ mol}^{-1}$ (C–C bond cleavage) and $62.8 \pm 1.0 \text{ kJ mol}^{-1}$ (dehydrogenation). Such low energy barriers under molecular flow conditions suggest activation steps that are obscured by higher-pressure catalysis.

Keywords Isobutane dehydrogenation · C–C bond cleavage · Kinetics · Flexible least squares

1 Introduction

Acidic zeolite substrates, such as HZSM-5 are vital catalysts in the petrochemical industry, due to high selectivity and activity outcomes. A monomolecular mechanism involving direct transfer of a Brønsted acid proton on the zeolite ($Z^-H_B^+$) to adsorbed alkanes to form carbocation intermediates is commonly suggested as the activation step [1, 2]. The role of carbonium ions in this mechanism has recently been confirmed for H/D exchange between deuterated zeolites and isoalkanes at room temperatures [3]. Alternative bimolecular mechanisms involve H_B^+ transfer to

an impurity or product alkene and then hydride transfer from a nearby alkane, or hydride abstraction from alkanes at Lewis acid sites [1, 2]. For isobutane reactions resultant carbonium ions lead to covalently bonded alkoxy species that subsequently evolve to gas-phase propene and isobutene. Concerted reaction dynamics have also been proposed and modelled [4]. Weak hydrogen bonding between C–H and O atoms on the zeolite has also been demonstrated to initiate low-temperature H/D exchange of isobutane with measured experimental activation energies [5, 6] of 57 and $50 \pm 2 \text{ kJ mol}^{-1}$ and theoretical values [7, 8] of 63 and 46.4 kJ mol^{-1} . Low-temperature activation for C–C bond cleavage to propene and methane, and dehydrogenation to isobutene and hydrogen of isobutane over acidic zeolites have not been previously reported.

2 Experimental

The rates of propene and isobutene evolution following exposure of isobutane to the zeolite HZSM-5 have been monitored using low-pressure, steady–steady, temperature-programmed reaction spectroscopy; a technique developed by this group [9, 10]. Isobutane molecules flow over the zeolite substrate located in a Knudsen cell reactor and gas-phase species evolving from the cell are directly monitored by a quadrupole mass spectrometer. Surface reactions are initiated as the temperature is raised linearly (5 °C min^{-1}) typically from 100 to 500 °C . Due to the short residence times in the cell, alkene product reactions and other secondary processes are unlikely. Heat fluctuations are also minimized and accurate rate data for the elementary steps to evolution from the solid surface are obtained. Figure 1 shows isobutene evolution rate data collected over three consecutive days. HZSM-5 was obtained from Zeolyst International (Kansas City, USA)

C. Le Minh
Faculty of Chemistry, Hanoi National University of Education,
136, Xuan Thuy Street, Cau Gay, HaNoi, Vietnam

A. K. Alanazi · D. J. Miron · T. C. Brown (✉)
School of Science and Technology, University of New England,
Armidale, NSW 2351, Australia
e-mail: trevor.brown@une.edu.au

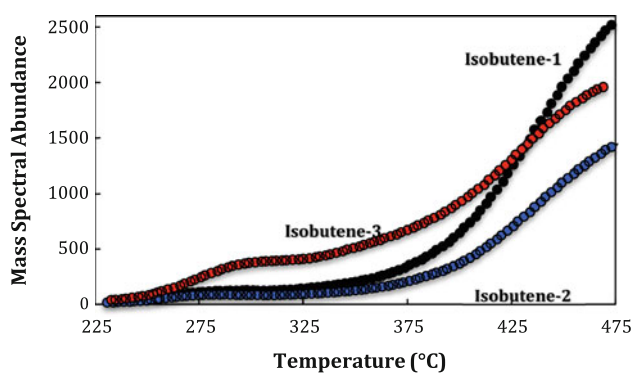


Fig. 1 Evolved isobutene during temperature-programmed activation of isobutane over HZSM-5, monitored over three consecutive days: Isobutene-1 (black circle), Isobutene-2 (violet circle) and Isobutene-3 (red circle)

and has unit cell formula $H_{5.48}(Si_{90.52}Al_{5.48})O_{189.3}$, SiO_2/Al_2O_3 ratio of 33.0 ± 1.8 and surface area of $358 \pm 10 \text{ m}^2 \text{ g}^{-1}$. Instrument grade isobutane (BOC Gases) was used without further purification.

The rate law for product evolution under low-pressure, steady-state conditions is

$$\begin{aligned} \frac{dN_{\text{product}}}{dt} (\text{molecules s}^{-1}) &= \frac{I_{\text{product}}}{\alpha_{\text{product}}} \\ &= \frac{A_2 Z I_{\text{isobutane}}}{A_{-1} \alpha_{\text{isobutane}}} \exp\left(\frac{-E_2 + \Delta H_{\text{ads}}}{RT}\right) \end{aligned} \quad (1)$$

Here, N_{product} are product molecules, I_{product} and $I_{\text{isobutane}}$ are mass-spectral abundances, α_{product} and $\alpha_{\text{isobutane}}$ are mass-spectral sensitivity factors, Z is the collision number per isobutane molecule, A_2/A_{-1} is the ratio of reaction and isobutane desorption pre-exponential factors, and $E_2 - \Delta H_{\text{ads}}$ is the reaction activation energy minus the enthalpy of isobutane adsorption (apparent activation energy, E_{app}). The apparent pre-exponential factor is

$$A_{\text{app}} (\text{collisions molecule}^{-1}) = \frac{A_2 \alpha_{\text{product}} Z}{A_{-1} \alpha_{\text{isobutane}}} \quad (2)$$

Combining these equations and taking natural logs leads to the simple linear equation

$$\ln I_{\text{product}}/I_{\text{isobutane}} = \ln A_{\text{app}} - E_{\text{app}}/RT \quad (3)$$

with unknown Arrhenius rate parameters $\ln A_{\text{app}}$ and E_{app} . These two parameters, however, cannot adequately simulate experimental gas–solid rate processes over a wide temperature range or surface coverage, due to lateral interactions between adsorbed species [11], mass and heat transfer effects [12], deactivation, surface heterogeneity and restructuring [13]. Such non-steady-state effects have previously been modelled for low-pressure temperature-programmed rate data, by introducing a third parameter or exponent, m for the coverage or isobutane abundance, i.e., $I_{\text{isobutane}}^m$ [9].

Recently, a time-varying flexible least squares [14–16] approach has been developed that simulates gas–solid rate data by calculating temperature-dependent activation energies, pre-exponential factors and differential conversion functions for the evolution of 3-methyl-2-oxetanone during the selective oxidation of isobutane over aluminium phosphomolybdates. Flexible least squares where modelled parameters evolve slowly and smoothly over time (or temperature) assumes that for any theoretical linear model proposed to explain observable data, there are two distinct types of discrepancy terms, dynamic and measurement. The dynamic terms account for time variation in successive parameter vectors, and the measurement terms account for differences between observed and theoretically predicted outcomes using linear regression. Optimization of the time-varying parameters is achieved by minimizing both the dynamic and the measurement residual squared errors. The result is a near perfect fit to the rate data.

3 Results and Discussion

The two rate parameters $\ln A_{\text{app}}(T)$ and $E_{\text{app}}(T)$ in Eq. (3) were optimized as a function of temperature, using flexible least squares for time-varying linear regression code provided by Kalaba and Tesfatsion [15] and adapted for the statistical computing language R [17]. Resultant temperature-dependent parameters are summarized in Table 1 for simulated C–C bond cleavage (evolved propene) and dehydrogenation (evolved isobutene) rate data. Temperature ranges over which the rates were simulated are also included in this table. Data sets were collected over three consecutive days using the same zeolite substrate, after exposure to a flow of O_2 at $500 \text{ }^\circ\text{C}$ for ca. 16 h, to remove any coke that may have deposited onto the zeolite surface during the previous run.

Table 1 Arrhenius rate parameters for evolved propene and isobutene calculated following temperature-programmed activation of isobutane over HZSM-5

Product-day	T -range ($^\circ\text{C}$)	$\log_{10} A_{\text{app}}^a$	E_{app} (kJ mol^{-1})
Propene-1	255–500	4.6 ± 0.3	71.59 ± 0.05
Propene-2	231–509	4.9 ± 0.2	72.85 ± 0.05
Propene-3	233–500	5.5 ± 0.4	77.24 ± 0.07
Combined mean		5.0 ± 0.9	73.9 ± 2.4
Isobutene-1	255–500	4.4 ± 0.5	61.26 ± 0.08
Isobutene-2	231–509	4.6 ± 0.4	63.45 ± 0.08
Isobutene-3	233–499	5.0 ± 0.3	63.43 ± 0.06
Combined mean		4.7 ± 0.7	62.8 ± 1.0

^a Units for A_{app} are isobutane collisions per evolved isobutene molecule

Errors in the parameters for individual data sets, listed in Table 1 are the calculated variations across each temperature range. The distribution of simulated apparent activation energies and pre-exponential factors for isobutene evolution are plotted in Figs. 2 and 3. The small errors and small graphical fluctuations demonstrate only a weak dependence on these parameters during each temperature-programmed run. The variations are likely to be due to mass-transfer limitations and deactivation. Errors listed in Table 1 for the combined means are the standard deviations across the three days and are significantly larger than individual errors and reflect the experimental error in the calculations.

Magnitudes of $\log_{10}A_{\text{app}}$ (5.0 ± 0.9 and 4.7 ± 0.7) are reasonable given that the ratio of mass-spectral sensitivity factors ($\alpha_{\text{product}}/\alpha_{\text{isobutane}}$) are 0.7 ± 0.4 for propene and 15.2 ± 10.0 for isobutene [9], collisions numbers (Z) [10] are typically 2550 ± 200 and A_{-1} is $10^{12 \pm 1} \text{ s}^{-1}$ [18]. Including these values in Eq. (2) gives intrinsic pre-exponential factors

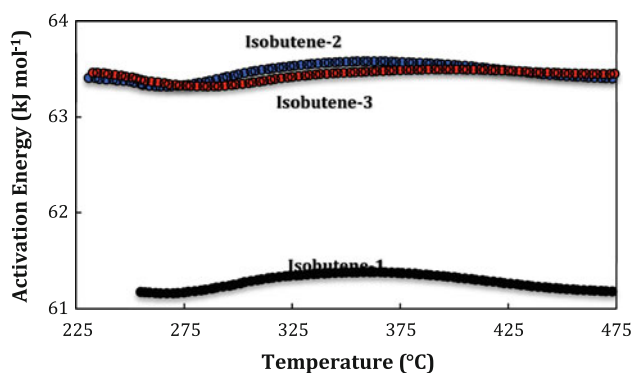


Fig. 2 Distribution of E_{app} for evolved isobutene during temperature-programmed activation of isobutane over HZSM-5, monitored over three consecutive days: Isobutene-1 (black circle), Isobutene-2 (violet circle) and Isobutene-3 (red circle)

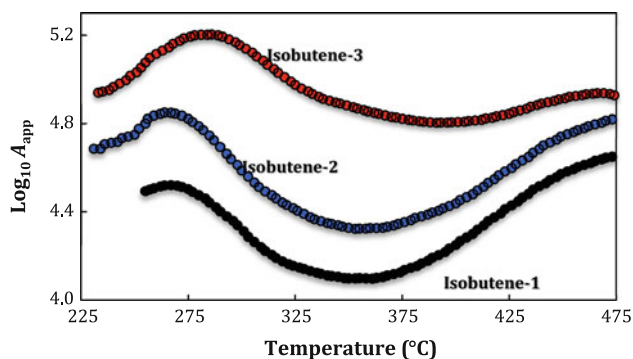


Fig. 3 Distribution of $\log_{10}A_{\text{app}}$ for evolved isobutene during temperature-programmed activation of isobutane over HZSM-5, monitored over three consecutive days: Isobutene-1 (black circle), Isobutene-2 (violet circle) and Isobutene-3 (red circle)

(A_2) of ca. $10^{13.7} \text{ s}^{-1}$ for C–C bond cleavage and ca. $10^{12.1} \text{ s}^{-1}$ for dehydrogenation.

Reported experimental and theoretical activation energies for isobutane C–C bond cleavage and dehydrogenation are generally much higher than the 73.9 ± 2.4 and $62.8 \pm 1.0 \text{ kJ mol}^{-1}$ calculated here. For example, recently Liu et al. [19], reported apparent activation energies of 194 ± 7 and $178 \pm 9 \text{ kJ mol}^{-1}$ for these two isobutane cracking pathways, determined to be monomolecular under the conditions of the experiment. These values also match theoretically calculated activation energies: 198 and 194 kJ mol^{-1} , respectively [20]. Previous calculations using the same low-pressure data sets, simulated in this letter, gave single apparent activation energies of $104.2 \pm 2.3 \text{ kJ mol}^{-1}$ (C–C cleavage) and $134.8 \pm 1.8 \text{ kJ mol}^{-1}$ (dehydrogenation) [9].

4 Conclusions

The unique low-pressure, molecular flow conditions used to investigate the rates of isobutane conversion and the calculation of temperature-dependent rate parameters have uncovered activation steps that are obscured during higher-pressure studies. Possible activation, under these conditions is via the formation of a surface complex that includes both weak hydrogen bonding between primary C–H and O on the zeolite and bonding between $Z^-H_B^+$ and C on the same methyl group. This stabilization could then lead to C–C bond cleavage and dehydrogenation. Such a mechanism has been previously modelled to give low activation energies of 63 and 46.4 kJ mol^{-1} for H/D exchange between isobutane and acidic zeolites [7, 8]. These theoretical barriers are similar in magnitude to the measured 57 kJ mol^{-1} reported for direct protium exchange [5] and the isobutane C–C bond cleavage and dehydrogenation energies of 73.9 ± 2.4 and $62.8 \pm 1.0 \text{ kJ mol}^{-1}$, measured here at low-pressures.

References

- Boronat M, Corma A (2008) Appl Catal A Gen 336:2–10
- Milas I, Silva AM, Nascimento MAC (2008) Appl Catal A Gen 336:17–22
- Sido ASS, Barbiches J, Sommer J (2012) Chem Commun 46: 2913–2914
- Pereira MS, da Silva AM, Nascimento MAC (2011) J Phys Chem C 115:10104–19113
- Truitt MJ, Toporek SS, Rovira-Truitt R, White JL (2006) J Am Chem Soc 128:1847–1852
- Sommer J, Habermacher D, Jost R, Sassi A, Stepanov AG, Luzzin MV, Freude D, Ernst H, Martens J (1999) J Catal 181:265–270
- Sremaniak LS, Whitten JL, Truitt MJ, White JL (2006) J Phys Chem B 110:20762–20764

8. Sukrat K, Tunega D, Aquino AJA, Lischka H, Parasuk V (2012) *Theor Chim Acta* 131:1232–1239
9. Le Minh C, Brown TC (2006) *Appl Catal A Gen* 310:145–154
10. Yanping S, Brown TC (2000) *J Catal* 194:301–308
11. Nieskens DLS, van Bavel AP, Niemantsverdriet JW (2003) *Surf Sci* 546:159–169
12. Budrugaec P, Segal E (2001) *Int J Chem Kinet* 33(10):564–573
13. Zhdanov VP, Kasemo B (1998) *J Stat Phys* 90(1/2):79–101
14. Kalaba R, Tesfatsion L (1989) *Comput Math Appl* 17(8/9): 1215–1245
15. Kalaba R, Tesfatsion L (1996) *Comput Stat Data Anal* 21: 193–214
16. Montana G, Triantafyllopoulos K, Tsagaris T (2009) *Expert Syst Appl* 36:2819–2830
17. R Core Team (2012). R: A language and environment for statistical computing. R Foundation for Statistical Computing, Vienna, Austria. ISBN 3-900051-07-0. <http://www.R-project.org/>
18. Pitt IG, Gilbert RG, Ryan KR (1995) *J Chem Phys* 102(8): 3461–3473
19. Liu D, Bhan A, Tsapatsis M, Al Hashimi S (2011) *ACS Catal* 1:7–17
20. Milas I, Nascimento MAC (2003) *Chem Phys Lett* 373:379–384