



Resolution of structural isomers of complex reaction mixtures in homogeneous catalysis



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ABSTRACT

Double-bond isomerization is a dominant side reaction in hydroformylation of long-chain linear olefins. This isomerization reaction was studied experimentally and theoretically using n-decenes as linear long-chain olefin representatives. On the experimental side, an isothermal batch isomerization experiment was carried out using Rh-BIPHEPHOS as catalyst until the reaction equilibrium was reached. Complete resolution and quantification of all n-decene isomers was achieved using gas chromatography. The observed equilibrium composition was used to extract Gibbs free energy changes of internal n-decenes relative to 1-decene. These were compared to (a) results based on Benson's group contribution method (BGCM) and (b) results from quantum mechanical (QM) calculations. Density functional theory (DFT: BP86, B3LYP, M06-2X) and second order Møller-Plesset (MP2) calculations showed a mean deviation to experimentally determined Gibbs free energy changes of 3–4 kJ mol⁻¹. Using dispersion correction (D3) in DFT calculations reduced the deviations by 1 kJ mol⁻¹. With a mean deviation of only 0.5 kJ mol⁻¹ for Gibbs free energy changes, BGCM was closer to experimental data. Entropy errors in QM calculations were estimated to be responsible for approx. 80% of Gibbs free energy errors.

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1. Introduction

Conversion of olefins by synthesis gas (H₂, CO) into aldehydes by cobalt, rhodium and palladium catalysts, known as hydroformylation, is one of the most important homogeneously catalyzed industrial processes [1]. This reaction delivers a broad product spectrum, ranging from terminal aldehydes to other side products such as branched aldehydes, olefin isomers, alkanes, alcohols and aldol condensation products [1]. The terminal aldehydes achieve a higher market price and are used for the production of plasticizers, odorants and surfactants, which makes them the desired product [1].

Recently, the hydroformylation of linear long-chain olefins was studied using a highly regioselective Rh-BIPHEPHOS catalyst [2,3].

In these studies, the catalyst was found to be very active towards double-bond isomerization of n-olefins (see Fig. 1), which occurs simultaneously to hydroformylation [4–9].

This isomerization reaction can either be regarded as an undesired side reaction leading to internal olefins and subsequently branched aldehydes or is essential for tandem isomerization-hydroformylation reaction sequences producing terminal aldehydes from cheap internal olefin mixtures or renewable oleochemicals with internal double-bonds [1,4–6,10–14]. The understanding and control of this isomerization reaction is important to increase the overall hydroformylation product yield with respect to the preferred terminal aldehydes.

Reliable physicochemical data for double-bond isomers of long-chain n-olefins and kinetic data regarding the double-bond isomerization are rare in the literature but necessary for a qualitative and quantitative understanding and description of this crucial side reaction. Thus, it is intended in this contribution to investigate the isomerization reaction of n-decenes experimentally and theoretically (a) to evaluate different theoretical approaches to calculate missing thermodynamic properties for n-olefin isomers and (b) to

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Nomenclature

Abbreviations

1d	1-decene
t2	<i>trans</i> -2-decene
t3	<i>trans</i> -3-decene
t4	<i>trans</i> -4-decene
t5	<i>trans</i> -5-decene
c2	<i>cis</i> -2-decene
c3	<i>cis</i> -3-decene
c4	<i>cis</i> -4-decene
c5	<i>cis</i> -5-decene
BGCM	Benson's group contribution method
DFT	density functional theory
GGA	generalized gradient approximation
MP2	second order Møller-Plesset
n-decenes	linear (or normal) decenes
QM	quantum mechanical
RMSE	root mean squared error
TMS	thermomorphic multicomponent solvent system
vib	vibrational

Constants

R	gas constant ($8.3145 \text{ J mol}^{-1} \text{ K}^{-1}$)
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Sub- and superscripts

\ominus	at standard pressure (1 bar) and standard temperature (298 K)
\circ	at standard pressure (1 bar)
i	component index
exp	experimental
eq	equilibrium
calc	calculated

Latin symbols

a	activity (mol l^{-1})
c_p	heat capacity ($\text{J mol}^{-1} \text{ K}^{-1}$)
E	electronic energy (kJ mol^{-1})
G	Gibbs free energy (kJ mol^{-1})
H	enthalpy (kJ mol^{-1})
K	equilibrium constant (-)
S	entropy ($\text{J mol}^{-1} \text{ K}^{-1}$)
T	temperature (K)
x	molar fraction (%-mol)

Greek symbols

γ_i	activity coefficient (-)
δ	error (-)

examine the isomerization kinetics qualitatively. The theoretical concepts applied are Benson's group contribution method (BGCM) and quantum mechanic (QM) calculations. Benson's group contribution method is easy to implement and does not require advanced computing power. However, the degree of structural complexity that can be distinguished with BGCM is limited. Thus, it is not possible to distinguish some n-decene isomers (*cis*-3-decene = *cis*-4-decene, *trans*-3-decene = *trans*-4-decene). Conformers of the same isomer are generally not considered in BGCM. Additionally, BGCM is depending on the experimental data to which the group contributions were fitted. To overcome this drawback of BGCM, several *ab initio* quantum chemistry methods to calculate thermodynamic properties of all individual n-decene isomers were tested. Regarding the QM methods, several DFT functionals (BP86, B3LYP, M06-2X) as well as the post-Hartree-Fock MP2 method were used.

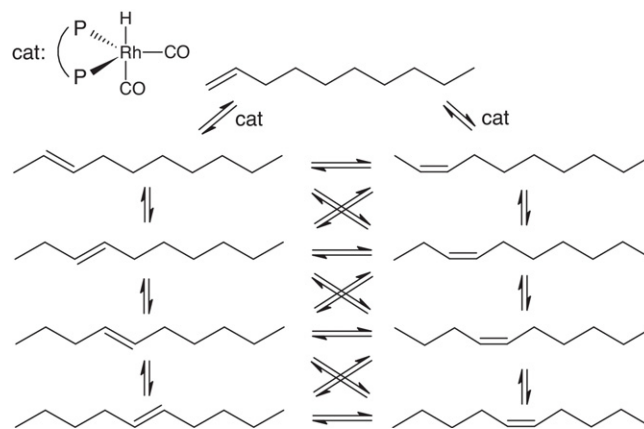


Fig. 1. Reaction network for the homogeneously catalyzed n-decene isomerization.

Since some authors point to the neglect of dispersion interactions as the dominating reason for systematic errors of the DFT methods, the effect of *a posteriori* dispersive corrections to the used DFT functionals on calculated thermodynamic properties was also examined.

The double-bond isomerization reaction of n-decene was investigated in the literature [15,16] but with a limited analytical resolution of the olefin isomers. Therefore, several n-olefin isomers were lumped into pseudo components. In this contribution, previous analytical limitations were overcome and the complete resolution of this complex reaction mixture was achieved. All n-decene isomers were detected, identified, calibrated and quantified with a new gas chromatographic setup analyzing batchwise 1-decene isomerization experiments using a Rh(BIPHEPHOS) catalyst. With this improved analytic setup, it was possible to follow the observed, time-resolved concentration courses of all n-decene isomers until no further changes in the concentration profiles were observed. From the observed final composition, Gibbs free energy changes of the n-decene isomers relative to 1-decene were calculated.

Thermodynamic properties of all n-decene isomers calculated with QM methods, such as enthalpy differences $\Delta \Delta_f H^\ominus$, entropies S^\ominus and Gibbs free energy differences $\Delta \Delta_f G^\ominus$, were compared to those from BGCM, whereas the calculated Gibbs free energy differences at reaction conditions $\Delta \Delta_f G^\circ$ (378 K) were directly compared to those extracted from experimental data and also to BGCM results.

2. Experimental details

The isomerization experiments were performed in a high pressure multi-reactor system (Parr Instrument Company) with a 75 ml pressure lock batch autoclave. Constructional details about the reactor setup can be found in the literature [16].

A thermomorphic multicomponent solvent system (TMS) [17] was used consisting of dodecane (Alfa Aesar >99%), dimethyl formamide (DMF, Merck > 99%) and 1-decene (Sigma Aldrich 94%) with the same molar composition that was used in [18] ($n_{\text{dec}}:n_{\text{dod}}:n_{\text{DMF}} = 1:3:4$, $n_{\text{dec}}^0 = 42.4 \text{ mmol}$). The n-olefins act as substrate and are part of the TMS at the same time, serving as a solubilizer. This solvent concept has the advantage of complete homogeneity at elevated reaction temperature without mass transfer limitations in the liquid phase, whereas at low temperature separation into two liquid phases (polar and nonpolar) occurs due to the thermodynamics of the ternary system [17]. The catalyst accumulates in the polar DMF phase while the product remains in the nonpolar phase, which allows elegant, energy efficient and careful catalyst recycling [19].

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