Kinetics of Carboxylic Acid Enolization on Metal Oxides in Vapor Phase

Alexey V. Ignatchenko, Reem Ibrahim, Jordan R. Kostera, Jordan D. Walker, Jared J. Jorolemon, Christian J. Leonardo*

Chemistry Department, St. John Fisher University, 3690 East Avenue, Rochester, NY 14618

Supporting Information

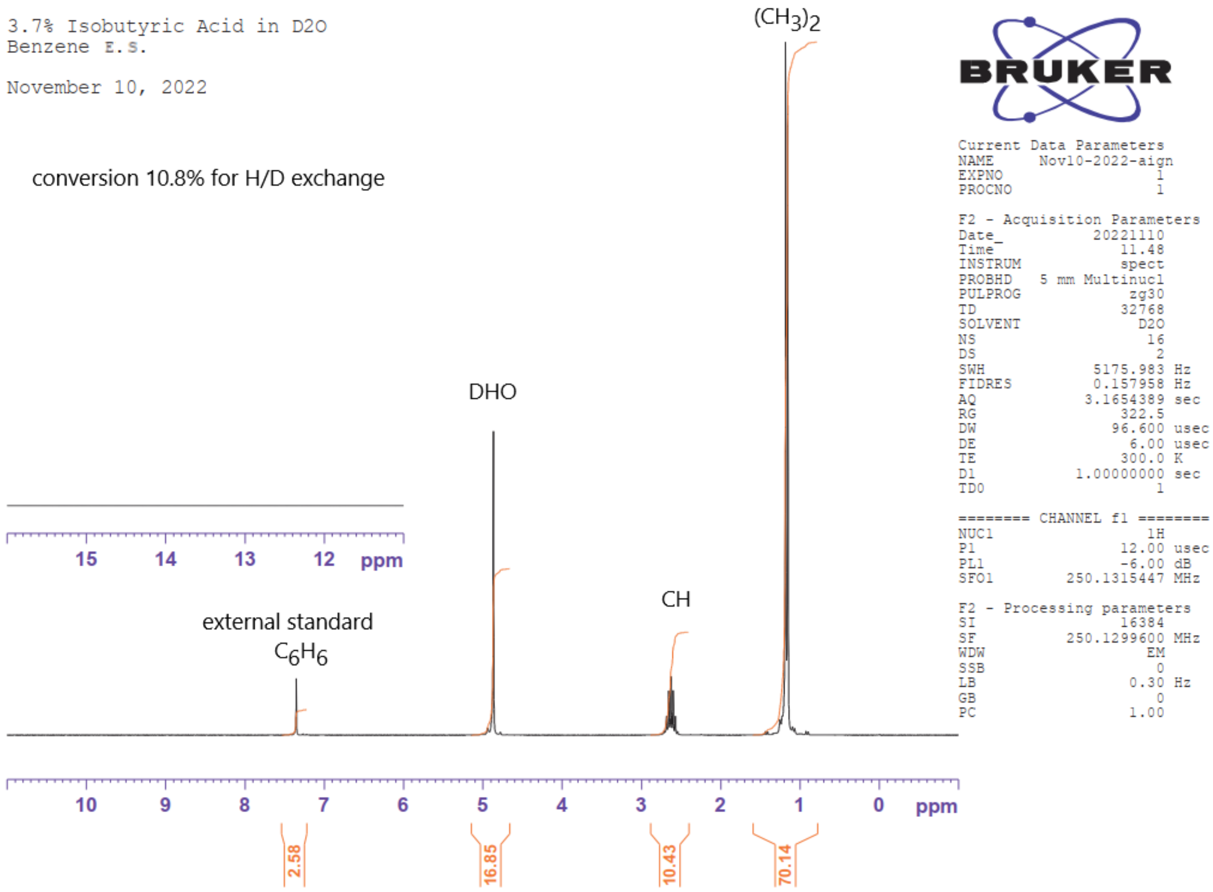
Table of Content

page

Section S1

Section S2

Section S1.



```
Current Data Parameters
NAME      Nov10-2022-aign
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_            20221110
Time                11.48
INSTRUM             spect
PROBHD   5 mm Multinucl
PULPROG              zg30
TD                  32768
SOLVENT               D2O
NS                     16
DS                      2
SWH              5175.983 Hz
FIDRES           0.157958 Hz
AQ              3.1654389 sec
RG                  322.5
DW                 96.600 usec
DE                   6.00 usec
TE                  300.0 K
D1             1.00000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                   1H
P1                  12.00 usec
PL1                 -6.00 dB
SFO1          250.1315447 MHz

F2 - Processing parameters
SI                  16384
SF            250.1299600 MHz
WDW                    EM
SSB                     0
LB                   0.30 Hz
GB                      0
PC                   1.00
```

Fig. S1. Typical ^{1}H NMR spectrum of isobutyric acid solution in D_2O.

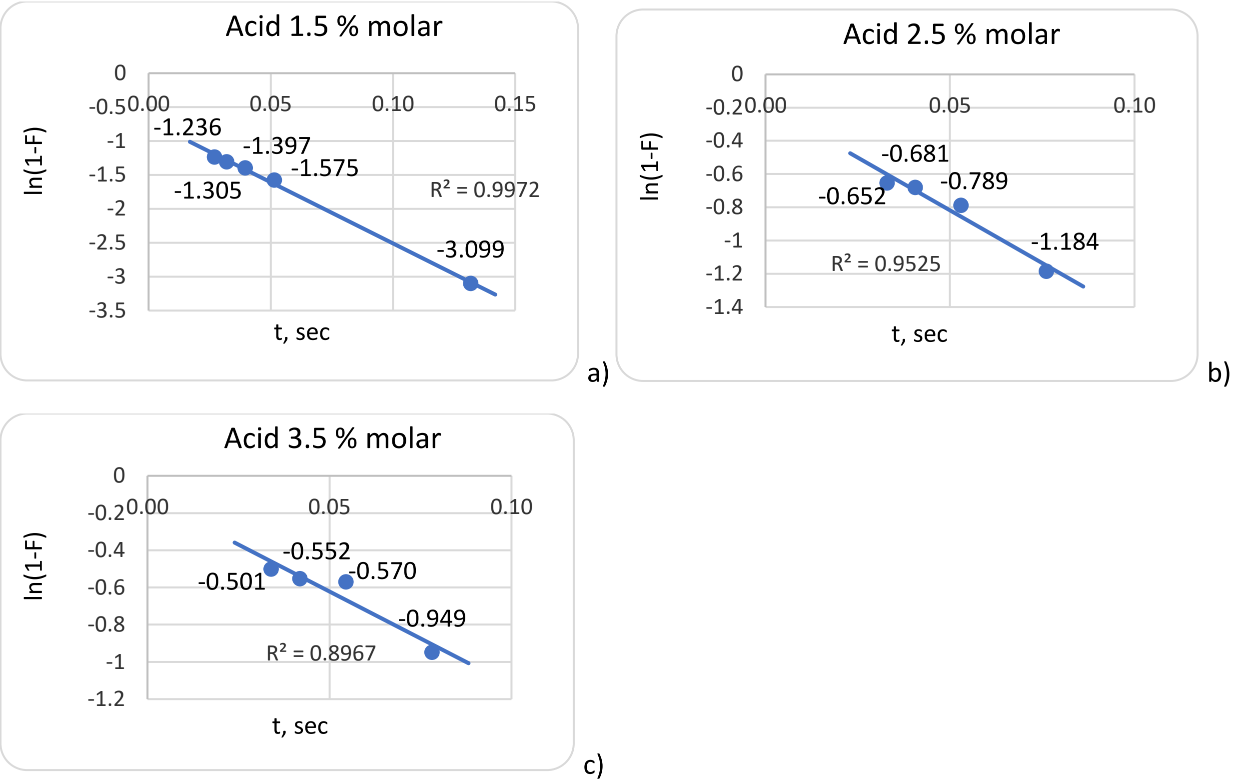


Fig. S2. Logarithmic plot of (1 - F) against time for an exchange experiment between isobutyric acid and D_2O at 220 °C temperature with ZrO_2 catalyst for various molar fractions of isobutyric acid, a) 1.5%, R_{ex}= 0.241 ± 0.007 b) 2.5%, R_{ex}= 0.283 ± 0.043 c) 3.5%, R_{ex}= 0.311 ± 0.074.

Table S1. Data for the calculation of R_{ex} for its dependance on isobutyric acid under pseudo-first-order conditions

P_A	P_X	Residence time	ln(1-F)	**R_{ex}**		
atm	atm	sec		**atm·sec^{-1}**		
0.0117	0.77	0.132	-3.0994			
0.0137	0.90	0.051	-1.57452			
0.0140	0.92	0.039	-1.39711			
0.0142	0.93	0.032	-1.30539			
0.0143	0.94	0.027	-1.23595	**0.241**	±	**0.007**
0.022	0.85	0.076	-1.184			
0.023	0.89	0.053	-0.78887			
0.023	0.91	0.041	-0.68112			
0.024	0.92	0.033	-0.65235	**0.283**	±	**0.043**
0.030	0.84	0.078	-0.94894			
0.032	0.88	0.055	-0.56988			
0.033	0.90	0.042	-0.55244			
0.033	0.91	0.034	-0.50086	**0.311**	±	**0.074**

Table S2. Data for the calculation of R_{ex} for its dependance on D_2O under pseudo-first-order conditions

P_A	P_X	Residence time	ln(1-F)	R_{ex}		
atm	atm	sec		**atm·sec^{-1}**		
0.695	0.029	0.165	-0.110			
0.747	0.031	0.133	-0.100			
0.781	0.033	0.112	-0.090			
0.806	0.034	0.096	-0.096			
0.840	0.035	0.075	-0.096	**0.0051**	±	**0.0024**
0.701	0.022	0.166	-0.097			
0.753	0.023	0.134	-0.092			
0.788	0.024	0.112	-0.089			
0.814	0.025	0.097	-0.071	**0.0072**	±	**0.0028**
0.620	0.013	0.220	-0.083			
0.707	0.014	0.167	-0.078			
0.795	0.016	0.113	-0.075			
0.821	0.017	0.097	-0.072			
0.841	0.017	0.085	-0.074			
0.760	0.016	0.135	-0.074	**0.0011**	±	**0.0002**

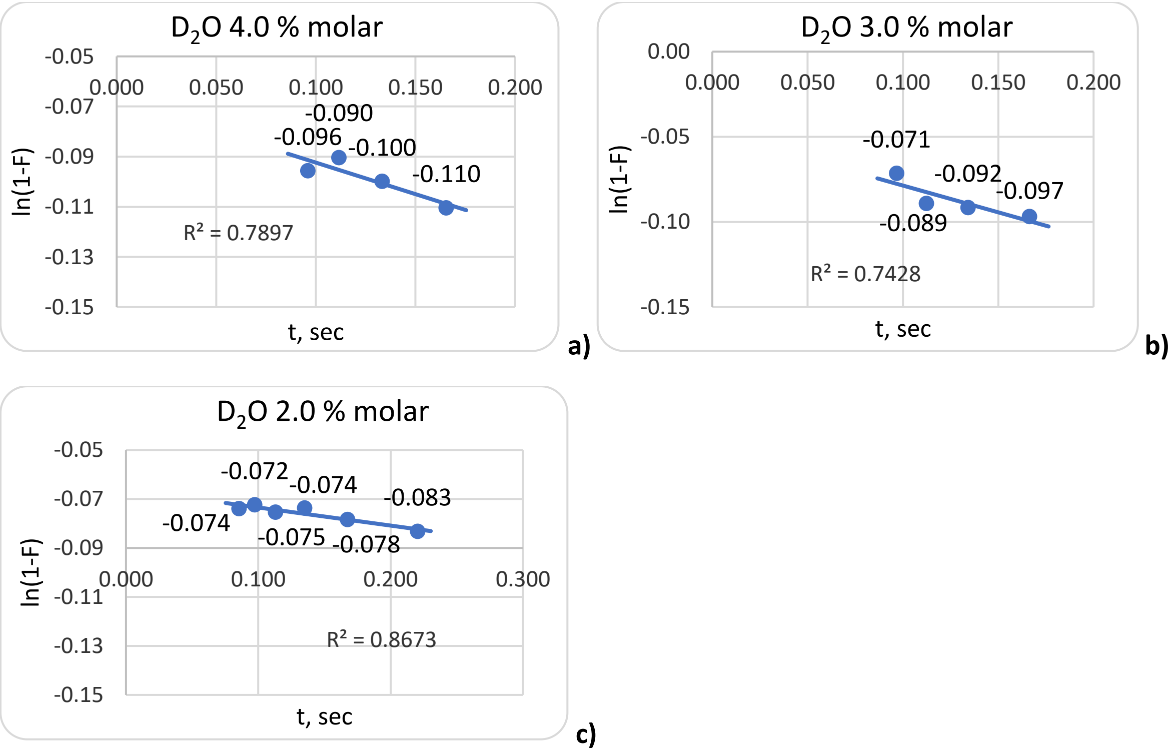


Fig. S3. Logarithmic plot of (1 - F) against time for an exchange experiment between isobutyric acid and D_2O at 220 °C temperature with ZrO_2 catalyst for various molar fractions of D_2O a) 4.0% b) 3.0% c) 2.0%.

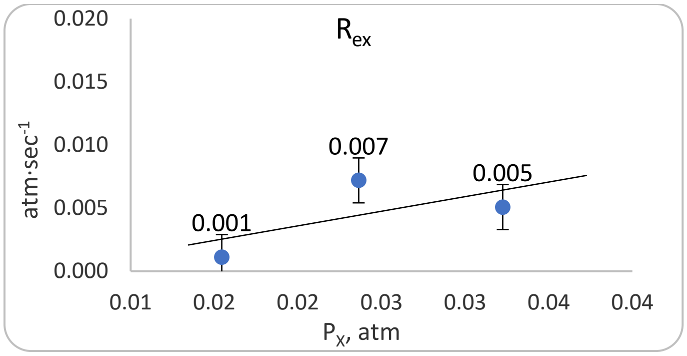


Fig. S4. R_{ex} (values listed in Table S2) shows scattering (no clear dependence on the partial pressure of D_2O) under pseudo-first-order conditions at approximately constant high partial pressure of isobutyric acid.

Section S2. Tests for the absence of diffusion limitations

Weisz-Prater criterion for the absence of internal diffusion limitations. Measurements of reaction rates were evaluated for the absence of external and internal mass transfer limitations. To evaluate possible internal mass transfer limitations, the Weisz-Prater criterion, C_{wp}, was calculated according to the next formula:

$$C_{wp} = \frac{r_{obs} R_p^2}{C_s D_e} \qquad \text{(S1)}$$

Where:

- C_{wp} = Weisz-Prater criterion (dimensionless).
- r_{obs} = observed reaction rate per unit volume of catalyst (mol/m³·s).
- R_p = radius of the catalyst particle (m).
- C_s = concentration of reactant at the external surface of the particle (mol/m³).
- D_e = effective diffusivity of the reactant in the porous catalyst (m²/s).

The effective diffusivity (D_e) was calculated from Knudsen diffusivity (D_{AB}) by the next equation:

$$D_e = \frac{D_{AB} \varphi_p \sigma_c}{\tau} \qquad \text{(S2)}$$

Where φ_p is pellet porosity, σ_c is constriction factor, and τ is tortuosity. Knudsen diffusivity (D_{AB}) was calculated by the next equation:

$$D_{AB} = \frac{d_{pore}}{3} \sqrt{\frac{8RT}{\pi M}} \qquad \text{(S3)}$$

where d_{pore} is the mean pore diameter, R is the ideal gas constant, and M is the molecule's molar mass.

Table S3. Tabulation of parameters for the calculation of mass transfer limitation for isobutyric acid H/D exchange with ZK catalyst at 200 °C temperature, 0.02 atm acid pressure.

Parameter	Value	Dimensionality
r_{obs}	11.366	$\mathrm{mol \cdot m^{-3} \cdot s^{-1}}$
R_p	0.00025	m
C_s	0.8929	$\mathrm{mol \cdot m^{-3}}$
D_e	1.5646E-05	$\mathrm{m^2 \cdot s^{-1}}$
D_{AB}	5.6895E-08	$\mathrm{m^2 \cdot s^{-1}}$
ϕp	1.1	$\mathrm{cm^3 \cdot g^{-1}}$
σc	1000	$\mathrm{kg \cdot m^{-3}}$
τ	4	dimensionless
d_{pore}	1.6E-08	m
R	8.31446262	$\mathrm{J \cdot mol^{-1} \cdot K^{-1}}$
T	473	K
M	88	amu
C_{wp}	0.051	dimensionless

The highest value of $C_{wp} = 0.051$ was found for ZK catalyst. Values for other catalysts, ZR, Ti, TK, were even smaller, 0.005, 0.037, 0.018, respectively. Since Weisz-Prater criterion, $C_{wp} << 1$, the measured reaction rate describes the catalytic reaction without being affected by internal mass transfer limitation phenomena.

Variation of the linear velocity at a constant residence time to test for the absence of external diffusion limitations. To check for any potential external diffusion limitations, the linear velocity of the gas feed was varied while keeping space time velocity (and the residence time) constant by adjusting the catalyst amount. No significant changes in the reaction rate were observed above velocity 10 m/sec, indicating that external mass transfer did not control the reaction rate (Fig. S4).

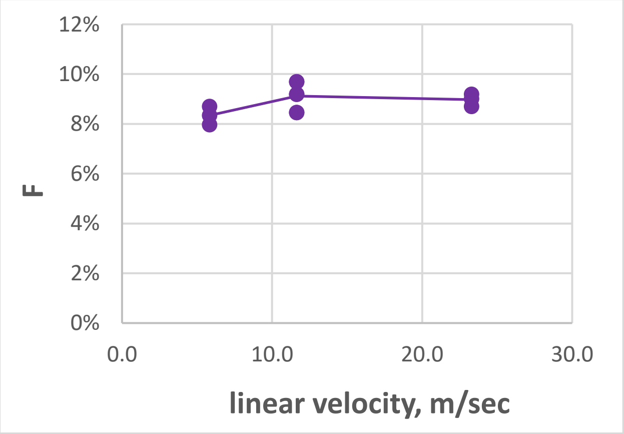


Fig. S5. Fraction of H/D exchange for isobutyric acid solution in D_2O with Ti catalyst at the temperature 200 °C measured in triplicate at the constant residence time, 0.0030 sec, at various linear velocities of the gas.

It was concluded that the system operated under kinetic control, with the observed reaction rates being controlled by the catalytic surface reactions rather than mass transport phenomena.