

## Kinetics and mechanism of hydrogenation of some olefins catalysed by anchored montmorillonitebipyridinepalladium(II) acetate

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**Abstract.** Kinetics of hydrogenation of some olefins such as 2,5-furandione, *cis*-butenedioic acid, *trans*-butenedioic acid, *cis*-methylbutenedioate and *trans*-methylbutenedioate catalysed by anchored montmorillonitebipyridinepalladium(II) acetate have been studied in THF medium. The observed rate was found to be first order with respect to partial pressure of hydrogen and fractional order with respect to both [catalyst] and [substrate]. The rate of hydrogenation follows the trend: 2,5-furandione > *cis*-butenedioic acid > *trans*-butenedioic acid > *cis*-methylbutenedioate > *trans*-methylbutenedioate. Thermodynamic parameters were evaluated, the rate law and a probable mechanism have been proposed.

**Keywords.** Olefin; catalytic hydrogenation; anchored catalyst; montmorillonite; kinetics of hydrogenation.

### 1. Introduction

The second half of the twentieth century saw a breakthrough in the field of catalysis with the technique of heterogenizing homogeneous catalysts by anchoring them to insoluble supports (Pittman 1980). Enhanced reaction rates were obtained when metal complex homogeneous catalysts were attached to a suitable support (Ermakov 1981). Such catalysts also offer advantages in recovery and recycling of the active species as well as enhanced specificity, though leaching cannot be avoided. The inorganic supports that have been explored include silica, alumina, glasses, zeolites and clay (Pinnavaia and Welta 1978). Of all these, clays are shown to be good supports. Smectite clay, which includes hectorite and montmorillonite, has greater potential as providing better catalyst support (Quale and Pinnavaia 1979). The intra-crystal space of the clay can be swelled by various solvents and the degree of swelling depends upon the interlayer cations, the substrate and negative charge density on the silicate sheet (Hartley 1985). Successful attempts were made to synthesize a series of montmorillonite functionalised palladium(II) complexes (Choudary *et al* 1985; Choudhary and Bharati 1987; Shimazu *et al* 1993). Even though mechanistic studies of hydrogenation of olefinic compounds were explored (Turkovich *et al* 1950; Bailor and Itatani 1967; Nayak *et al* 1985) very little attention has been paid to the kinetic study for understanding the mechanism. Here we report the hydrogenation of a series of olefins, namely 2,5-furandione, *cis*-butenedioic acid, *trans*-butenedioic acid, *cis*-methylbutenedioate

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and *trans*-methylbutenedioate catalysed by anchored montmorillonitebipyridinepalladium(II) acetate.

## 2. Experimental

### 2.1 Materials

Montmorillonite ( $1.2 \text{ meq g}^{-1}$ ) employed in the system was obtained from Fluka chemicals, Switzerland. Bipyridine and silicone rubber septa (14 joint) white were obtained from Aldrich, USA. Palladium acetate was obtained from Alchem Laboratories (India). *n*-Butyl lithium was obtained from E Merck (Germany). All other chemicals were obtained from S D Fine Chemicals (India). Air- and moisture-sensitive reactions were carried out in an inert atmosphere. All reagents have been either recrystallised or distilled, wherever necessary by adopting standard methods reported in the literature (Vogel 1979).

### 2.2 Measurements

The catalyst was prepared according to the procedure cited in the literature (Choudary and Bharati 1987) and the hydrogenation kinetics was carried out using a specially fabricated system. Hydrogen was purified by passing over a deoxo catalyst, through molecular sieves and drying tubes, before admission into the vacuum system. Hydrogenation reactions were carried out in a 100 ml two-necked round-bottomed flask. The side arm was packed with a silicone rubber septa and the other arm attached to a glass vacuum manifold equipment with a manometer, a gas burette, and a gas-inlet. A weighed amount of the catalyst was placed in the reaction vessel and was attached to the reaction system. To this, 10 ml of dry THF was added and the whole system was evacuated and flushed three times with pure hydrogen. The mixture was shaken for 30 minutes in the presence of hydrogen. A weighed amount of substrate (olefin) in a measured quantity of solvent was injected into the pre-equilibrated reaction system. The speed of shaking was regulated to ensure that the reaction rate did not depend on the shaking. Hydrogen uptake commenced without any induction period. The rate of hydrogen uptake was monitored at regular time intervals. At the end of each run, the catalyst was separated by filtration and thoroughly washed with dry THF. The filtrate was spectroscopically analysed by IR and NMR for qualitative identification of reaction products. To carry out the reaction at different temperatures a thermostat or cryostat was used and water circulated through the outer jacket of the system.

## 3. Results and discussion

The stoichiometry of the reaction was determined by maintaining an excess of hydrogen with the olefin (substrate) for several hours and measuring the hydrogen consumed. It was found that the total hydrogen consumption corresponds to complete hydrogenation of the carbon-carbon double bond that was present in the substrate. The stoichiometry was found to be 1:1 (substrate:hydrogen). The hydrogenated products were spectroscopically confirmed by IR and NMR.

The relative rates of various substrates have been presented in table 1. The plot of  $\log V$  versus  $\log[\text{substrate}]$  gave a straight line with a positive slope, indicating a fractional order dependence on the substrate concentration for all substrates. The order of reactivities of various substrates were found to be 2,5-furandione > *cis*-butenedioic acid > *trans*-butenedioic acid > *cis*-methylbutenedioate > *trans*-methylbutenedioate.

**Table 1.** Effect of [substrate] on reaction rates at three different temperatures.  
 Reaction conditions: [catalyst]:0.40 × 10<sup>-2</sup> m mol,  $p_{H_2}$ :1.063 × 10<sup>2</sup> kNm<sup>-2</sup>; solvent: THF; all temperatures in kelvin

[S] × 10 <sup>2</sup> (m mol)	Rate × 10 <sup>3</sup> m mol s <sup>-1</sup>														
	2,5-Furandione			cis-Butene dioic acid			trans-Butene dioic acid			cis-Methyl butenedioate			trans-Methyl butenedioate		
	288	300	306	288	300	306	288	300	306	288	300	306	288	300	306
0.50	0.55	0.66	0.74	0.49	0.55	0.58	0.47	0.53	0.57	0.28	0.33	0.38	0.29	0.31	0.35
1.00	0.72	0.92	1.03	0.64	0.76	0.83	0.63	0.74	0.80	0.37	0.47	0.52	0.37	0.44	0.49
2.00	0.90	1.13	1.26	0.81	0.95	1.03	0.80	0.92	1.02	0.45	0.56	0.63	0.43	0.56	0.62
2.50	0.94	1.18	1.42	0.85	1.02	1.17	0.84	1.01	1.15	0.47	0.62	0.71	0.48	0.57	0.67
3.00	0.97	1.30	1.49	0.89	1.11	1.23	0.88	1.10	1.21	0.48	0.65	0.74	0.49	0.62	0.71
4.00	1.07	1.41	1.68	1.01	1.21	1.40	0.92	1.23	1.37	0.51	0.72	0.78	0.51	0.69	0.76

**Table 2.** Effect of [catalyst] on reaction rates.  
 Reaction conditions: [substrate]:1.00 × 10<sup>-2</sup> m mol, P<sub>H<sub>2</sub></sub>:1.063 × 10<sup>2</sup> kNm<sup>-2</sup>; solvent: THF; all temperatures in kelvin

[C] × 10 <sup>2</sup> (m mol)	Rate × 10 <sup>3</sup> m mols <sup>-1</sup>														
	2,5-Furandione			cis-Butene dioic acid			trans-Butene dioic acid			cis-Methyl butenedioate			trans-Methyl butenedioate		
	288	300	306	288	300	306	288	300	306	288	300	306	288	300	306
0.15	0.40	0.46	0.52	0.33	0.37	0.40	0.33	0.39	0.41	0.20	0.24	0.26	0.21	0.24	0.26
0.20	0.48	0.59	0.64	0.40	0.46	0.49	0.42	0.47	0.50	0.25	0.30	0.32	0.25	0.29	0.31
0.25	0.55	0.69	0.75	0.47	0.53	0.57	0.67	0.54	0.59	0.28	0.35	0.37	0.29	0.34	0.36
0.30	0.62	0.76	0.83	0.53	0.63	0.67	0.54	0.62	0.65	0.31	0.38	0.43	0.30	0.37	0.41
0.40	0.72	0.92	1.03	0.65	0.76	0.83	0.63	0.74	0.80	0.37	0.47	0.52	0.37	0.44	0.48
0.50	0.80	1.06	1.19	0.73	0.90	0.96	0.72	0.85	0.93	0.41	0.54	0.59	0.41	0.51	0.55

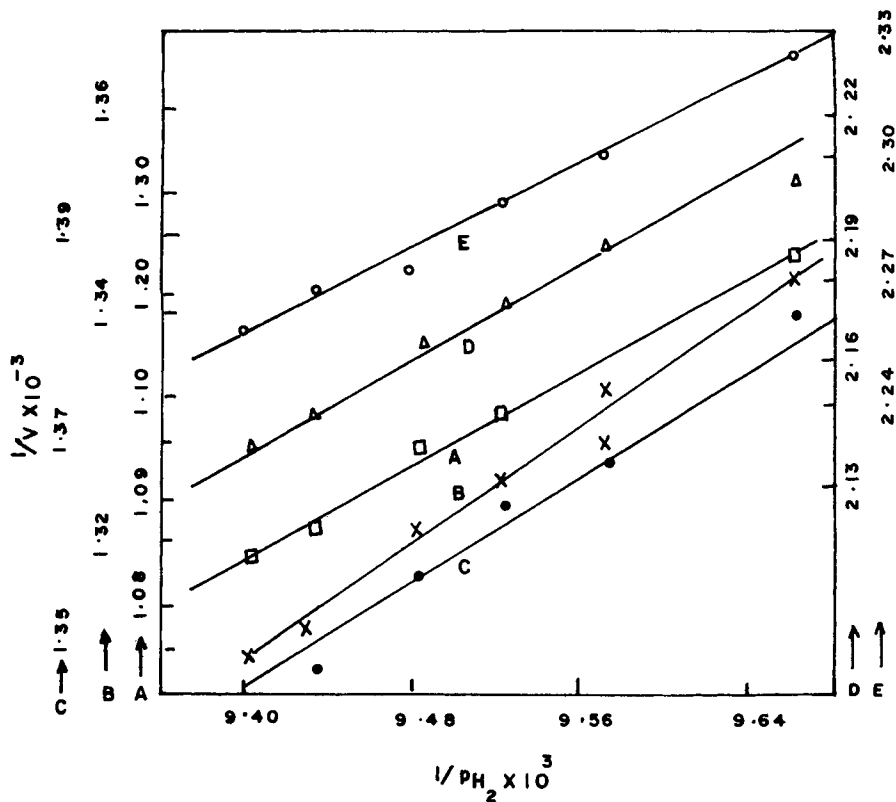
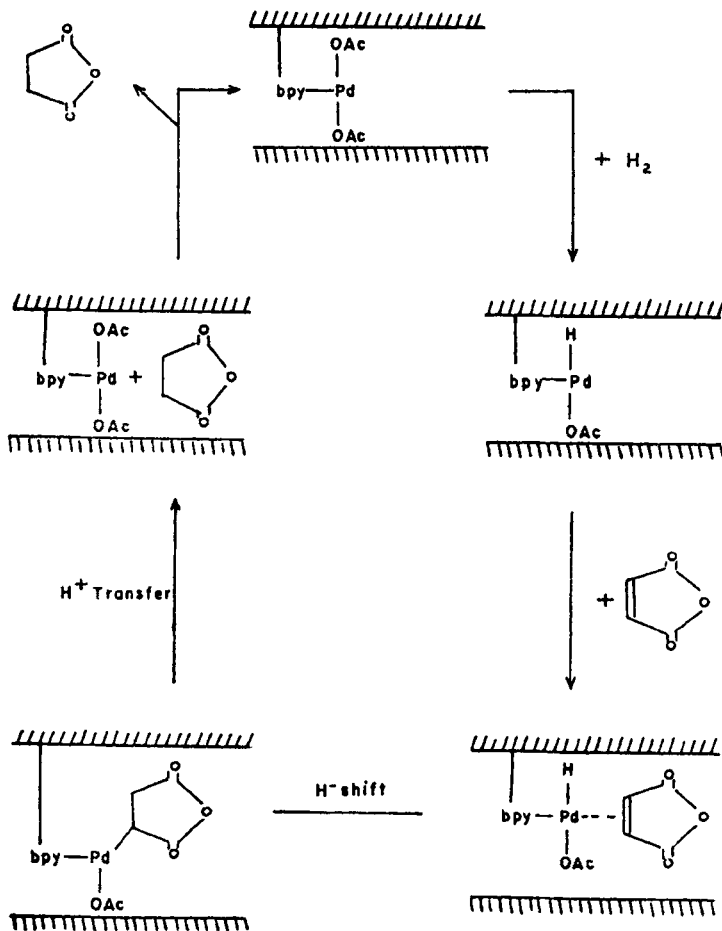


Figure 1. Plot of  $1/V$  vs  $1/p_{H_2}$ . A—2,5-furandione; B—*cis*-butenedioic acid; C—*trans*-butenedioic acid; D—*cis*-methyl butenedioate; E—*trans*-methyl butenedioate.

Rates of hydrogenation were found to be proportional to the catalyst concentration (table 2). The increase in concentration of the catalyst lead to increase in reaction rates. The plots of  $\log V$  versus  $\log[\text{catalyst}]$  indicated fractional order dependence on the catalyst concentration. The plot of  $\log V$  versus  $\log p_{H_2}$  indicated first order dependence on partial pressure of hydrogen. Formation of intermediate hydride species may be indicated in reversible equilibrium step. Plots of reciprocal rates versus reciprocal hydrogen partial pressure were linear with intercepts on the rate axis (figure 1). The error limits are  $\pm 3\%$ .

Based on the above data the following mechanism is proposed which is in accordance with the one proposed by Turkovich (1950) for hydrogenation of ethylene in heterogenous catalysis involving palladium, represented by (1)–(3) below and scheme 1.





**Scheme 1.** Probable mechanism for hydrogenation of 2,5-furandione.

Thus the mechanism involves the initial complex ( $C_1$ ) formation between catalyst (C) and hydrogen involving hydride ion transfer to the palladium, replacing the acetate ion. In the second equilibrium step, initially olefin (S) forms a  $\pi$ -complex ( $C_2$ ) with the palladium, and hydride ion transfer simultaneously takes place from palladium to olefin. The last step is rate-determining, which involves the transfer of proton to substrate leading to the separation of the hydrogenated product from the catalyst. Thus the catalyst is regenerated.

The rate law derived is as follows:

$$-\frac{d[S]}{dt} = -\frac{dp_{H_2}}{dt} = V = \frac{kK_1K_2[C]p_{H_2}[S]}{1 + K_1[C] + K_2[S] + K_1K_2[C][S]} \quad (4)$$

This equation accounts for the first order dependence on  $p_{H_2}$  and fractional order dependence on both [catalyst] and [substrate].

**Table 3.** Thermodynamic parameters at 300 K involving equilibrium constant  $K_1$  (values in parentheses were calculated using  $K_2$ ).

Parameters	2,5-Furandione	<i>cis</i> -Butene-dioic acid	<i>trans</i> -Butene-dioic acid	<i>cis</i> -Methyl butenedioate	<i>trans</i> -Methyl butenedioate
$-\Delta G$ (kJ mol <sup>-1</sup> )	13.1 (12.2)	12.2 (11.8)	13.1 (11.7)	13.2 (12.3)	13.5 (12.2)
$-\Delta H$ (kJ mol <sup>-1</sup> )	20.7 (15.5)	22.4 (15.7)	17.6 (15.8)	20.6 (19.2)	17.3 (18.6)
$-\Delta S$ (J mol <sup>-1</sup> K <sup>-1</sup> )	25.4 (11.1)	34.3 (12.8)	14.9 (13.4)	24.7 (23.0)	12.7 (21.3)

**Table 4.** Activation parameters at 300 K.

Parameters	2,5-Furandione	<i>cis</i> -Butene dioic acid	<i>trans</i> -Butene dioic acid	<i>cis</i> -Methyl butenedioate	<i>trans</i> -Methyl butenedioate
$E_a$ (kJ mol <sup>-1</sup> )	32.8	32.6	27.4	32.9	29.9
$\Delta G^\ddagger$ (kJ mol <sup>-1</sup> )	58.8	58.6	59.2	60.7	61.0
$\Delta H^\ddagger$ (kJ mol <sup>-1</sup> )	30.4	30.1	24.9	30.4	27.5
$-\Delta S^\ddagger$ (J mol <sup>-1</sup> K <sup>-1</sup> )	95.0	95.0	115.0	100.8	111.7

In order to evaluate the individual equilibrium and rate constants  $K_1$ ,  $K_2$  and  $k$ , (4) is modified in terms of  $k'$ , the pseudo first order rate constant at constant hydrogen partial pressure,

$$k' = \frac{V}{p_{H_2}} = \frac{kK_1K_2[C][S]}{1 + K_1[C] + K_2[S] + K_1K_2[C][S]} \quad (5)$$

Taking reciprocals of (5)

$$\frac{1}{k'} = \frac{1}{kK_1K_2[C][S]} + \frac{1}{kK_2[S]} + \frac{1}{kK_1[C]} + \frac{1}{k} \quad (6)$$

A plot of  $1/k'$  versus  $1/[S]$  gave a straight line with a positive intercept and slope supporting the proposed reaction scheme and enabling the evaluation of  $K_2$  from the ratio of intercept and slope. Similarly the plot of  $1/k'$  versus  $1/[C]$  also gave a straight line with a positive slope. The ratio of intercept and slope gave the value of  $K_1$ . The reaction was studied at different temperatures and the corresponding thermodynamic and activation parameters were evaluated (tables 3 and 4).  $\Delta G$  is negative for both equilibrium steps indicating the spontaneity of the complex formation. However, the complex formation between the catalyst and hydrogen seems to be more favourable. Also both  $\Delta H$  and  $\Delta S$  are negative for the formation of the complexes. Even though the

energy of activation of hydrogenation of 2,5-furandione is more than that of other substrates, the secondary electronic effects seem to favour the reaction leading to higher rates. Another feature is that the *cis*-olefins (*cis*-butenedioic acid and *cis*-methylbutenedioate) are found to be hydrogenated more readily than the *trans*-olefins (*trans*-butenedioic acid and *trans*-methylbutenedioate). In general, it may be concluded that *cis*-alkene is more readily coordinated than the *trans*-alkene in the interlayers of the montmorillonite, with the implication that the release of strain energy contributes to coordination. Thus the preferential rate of hydrogenation is in the order 2,5-furandione > *cis*-butenedioic acid > *trans*-butenedioic acid > *cis*-methylbutenedioate > *trans*-methylbutenedioate, which can be attributed to preferential complexation with the *cis*-isomer over the *trans*-isomer in the interlayers of montmorillonite. Thus the lower rate of hydrogenation of esters, namely *cis*-methylbutenedioate and *trans*-methylbutenedioate, is obvious.

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