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Anchored Montmorillonite Diphenyl Phosphino Palladium(II) Chloride Mediated Hydrogenation of Maleic Anhydride and Its Related Geometric Isomers: A Kinetic Study

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A kinetic study of hydrogenation of maleic anhydride and few related geometrical isomers has been carried out with anchored montmorillonite diphenyl phosphino palladium(II) chloride as the catalyst in the temperature range of 288-306 K. Reaction kinetics indicated first order dependence on [H_2]. A mechanism consistent with the experimental data has been proposed. The activation and thermodynamic parameters have been evaluated.

Key Words: Hydrogenation, Maleic anhydride, Maleic acid, Fumaric acid, Methyl maleate, Methyl fumarate, Ethyl maleate, Ethyl fumarate.

INTRODUCTION

Kinetics of chemical reactions provides an excellent tool to understand the mechanism of chemical transformation[1-5], which could be attributed to two important features. First feature could be the practical importance of being able to predict the nature of equilibrium. Rate of the reaction could be controlled by the variables such as pressure, temperature and the presence of a catalyst. This feature also provides a clue to optimize the reaction condition. The second feature leads to an understanding of the mechanism of a reaction whether the reaction occurs in a single step or involves a sequence of elementary steps.

Maleic anhydride[6] and maleic acid upon hydrogenation gave succinic anhydride and succinic acid, respectively. Both the products are used as intermediates in chemical, pharmaceutical and food industries[6-9]. Succinic acid occurs naturally in plant and animal tissues and plays a significant role in intermediary metabolism (Krebs's cycle). As a drug it is used as sedative, antispasmodic, antiphlegm, antiphogistic, contraceptive and in cancer treatment. In food industries it is used in beverages and as a flavoring agent. It is also used as an intermediate in the synthesis of dyes, perfumes, lacquers, alkyd resins *etc*. Succinic anhydride is mainly used in the manufacture of polymeric materials such as alkyd and special resins. It is also used as a cross linking agent in ion exchange membranes, curing agent for epoxy resins and starch modifiers in foods and feeds. In view of this the authors have chosen maleic anhydride and related geometrical isomers such as maleic acid, fumaric acid, methyl maleate, methyl fumarate, ethyl maleate and ethyl fumarate as substrates. In reaction kinetics activation of molecules plays a major role in the direction of product formation. Small molecules can be activated more conveniently than heavy molecules.

EXPERIMENTAL

Anchored montmorillonite diphenylphosphino palladium(II) chloride was prepared according to the literature procedures[10]. Air and moisture sensitive reactions were carried out with the use of standard inert atmosphere techniques. Tetrahydro furan was dried and deoxygenated by distilling over sodium benzophenone in nitrogen atmosphere. The substrates for hydrogenation were obtained from Aldrich. Montmorillonite clay was obtained from Fluka. Hydrogen gas employed was purified by passing over a deoxo catalyst, through molecular sieves and drying tubes before admission into the vacuum system.

Procedure: Hydrogenation reactions were carried out in a 100 mL two necked round bottomed flask. The side arm was packed with a silicone rubber septum and the other neck is attached through a three-way stopcock, which was connected to a glass vacuum, which in turn is equipped with a manometer, a gas burette and a gas-inlet. A known amount of the catalyst was placed in a reaction vessel and was attached to a reaction system. To this 10 mL of dry THF was added and the whole system is evacuated and flushed few times with pure hydrogen. The catalyst was activated by shaking it for 0.5 h in presence of hydrogen followed by inducting a known amount of substrate into it. The rate of hydrogen uptake was monitored at regular time intervals. Throughout the reaction, the reaction mixture is kept for shaking at a speed, which does not affect the rate of the reaction. The products were analyzed by NMR spectroscopic methods. The uptake of hydrogen was plotted by initial rate method to obtain rate in mL/min, which is converted to mol dm^{-3} units under STP conditions.

Maleic anhydride, maleic acid, methyl maleate, ethyl maleate, fumaric acid, methyl fumarate and ethyl fumarate were taken to study the kinetics of hydrogenation. The study was carried out at different temperatures in the range 288-306 K.

RESULTS AND DISCUSSION

Stoichiometry: The stoichiometry of the reaction was determined at different concentrations of the substrate. Keeping all other conditions constant hydrogenation of the olefin was carried out for several hours and the consumed hydrogen was measured. The stoichiometry of the reaction was found to be [substrate]: $^{P}H_2$ as 1:1.

Effect of [catalyst]: The hydrogenation was carried out as a function of catalyst concentration, which was varied in the range 0.15×10^{-2}-0.50×10^{-2} mol dm^{-3} three different temperature *viz.*, 288, 300 and 306 K. As the concentration of catalyst was increased the rate of hydrogenation for the above substrates also increased. A logarithmic plot of rate (V) *versus* concentration of the catalyst [C] gave a positive slope less than unity and greater than zero (Fig. 1) indicating fractional order with respect to [catalyst] (Table-1).

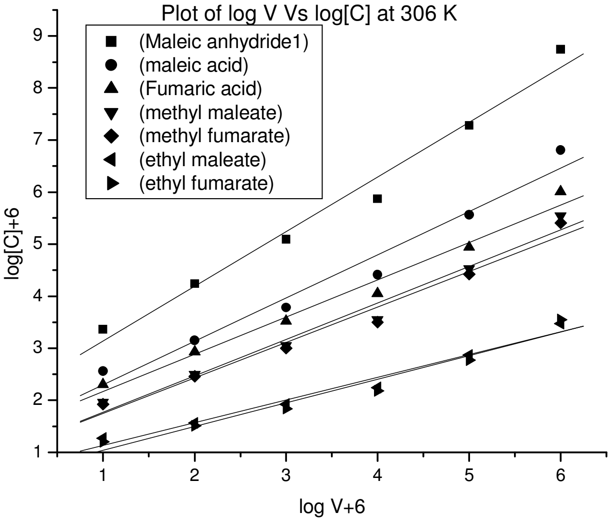


Fig. 1. Plot of log V *versus* log [C]

Effect of [substrate]: Hydrogenation was carried out with respect to the different concentrations of the substrates keeping the catalyst concentration and pressure of hydrogen constant at three different temperatures. The substrate concentration was varied in the range 0.15 × 10^{-2} to 4 × 10^{-2} mol dm^{-3} at 288, 300 and 306 K. With an increase in substrate concentration rate of hydrogenation increased significantly (Fig. 2). A linear graph with a slope (n) less than unity (1 > n > 0) was obtained when log V (where V = rate) values were plotted as a function of log [substrate] indicating fractional order with respect to [substrate] (Table-2).

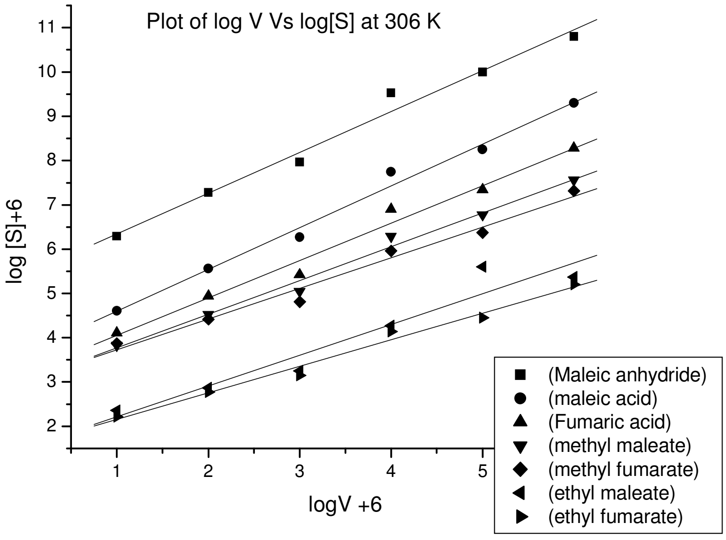


Fig. 2. Plot of log V *versus* log [S]

TABLE-1
EFFECT OF [CATALYST] ON REACTION RATES
Reaction conditions: 10^5 [substrate]: 0.75 mol dm^{-3}; 10^{-2} $^{P}H_2$: 1.063 kNm^{-2}; Solvent: THF; Temperature: 288-306 K; Rate X 10^6 mol dm^{-3} s^{-1}

	Maleic anhydride			Maleic acid			Fumaric acid			Methyl maleate			Methyl fumarate			Ethyl maleate			Ethyl fumarate		
10^5 [C] mol dm^{-3}	Temperature (K)																				
	288	300	306	288	300	306	288	300	306	288	300	306	288	300	306	288	300	306	288	300	306
0.150	3.15	3.31	3.36	2.44	2.51	2.56	2.15	2.22	2.30	1.91	1.92	1.96	1.82	1.89	1.92	1.05	1.21	1.27	0.98	1.17	1.20
0.200	3.87	4.06	4.24	3.00	3.15	3.15	2.50	2.72	2.93	2.23	2.38	2.50	2.24	2.33	2.46	1.29	1.48	1.56	1.26	1.44	1.51
0.250	4.54	4.88	5.09	3.54	3.64	3.78	3.04	3.21	3.52	2.81	2.91	3.05	2.74	2.84	3.00	1.54	1.80	1.92	1.48	1.77	1.84
0.300	5.16	5.63	5.87	4.09	4.35	4.41	3.54	3.74	4.05	3.29	3.46	3.55	3.25	3.40	3.50	1.78	2.10	2.24	1.72	2.06	2.18
0.400	6.23	7.05	7.28	5.02	5.39	5.56	4.44	4.71	4.94	4.20	4.34	4.53	4.05	4.32	4.42	2.16	2.64	2.87	2.12	2.56	2.77
0.500	7.36	8.49	8.74	5.98	6.38	6.81	4.88	5.53	6.01	4.96	5.11	5.54	4.84	5.05	5.41	2.63	3.20	3.47	2.52	3.12	3.55

TABLE-2
EFFECT OF [SUBSTRATE] ON REACTION RATES
Reaction conditions: 10^5 [catalyst]: 0.40 mol dm^{-3}; 10^{-2} $^{P}H_2$: 1.063; Solvent: THF; Temperature: 288-306 K

	Maleic anhydride			Maleic acid			Fumaric acid			Methyl maleate			Methyl fumarate			Ethyl maleate			Ethyl fumarate		
10^5 [S] mol dm^{-3}	Temperature (K)																				
	288	300	306	288	300	306	288	300	306	288	300	306	288	300	306	288	300	306	288	300	306
0.500	5.50	6.18	6.29	4.37	4.61	4.61	4.04	4.05	4.11	3.74	3.83	3.83	3.62	3.81	3.87	1.95	2.22	2.36	1.87	2.13	2.22
0.750	6.23	7.05	7.28	5.02	5.39	5.56	4.44	4.71	4.94	4.20	4.34	4.53	4.05	4.32	4.42	2.16	2.64	2.87	2.12	2.56	2.77
1.000	6.85	7.59	7.97	5.55	5.99	6.27	4.88	5.18	5.42	4.62	4.83	5.05	4.42	4.66	4.81	2.41	2.96	3.25	2.40	2.90	3.15
2.000	8.16	8.88	9.53	6.66	7.38	7.75	6.07	6.47	6.90	5.72	6.02	6.29	5.38	5.69	5.96	3.04	3.76	4.27	3.10	3.78	4.14
2.500	8.53	9.31	10.0	7.06	7.82	8.25	6.50	6.88	7.34	6.15	6.47	6.78	5.76	6.04	6.37	3.25	4.04	5.60	3.35	4.04	4.45
4.000	9.18	9.96	10.8	7.66	8.69	9.30	7.33	7.66	8.28	6.87	7.04	7.56	6.51	6.68	7.32	3.62	4.55	5.37	3.85	4.61	5.20

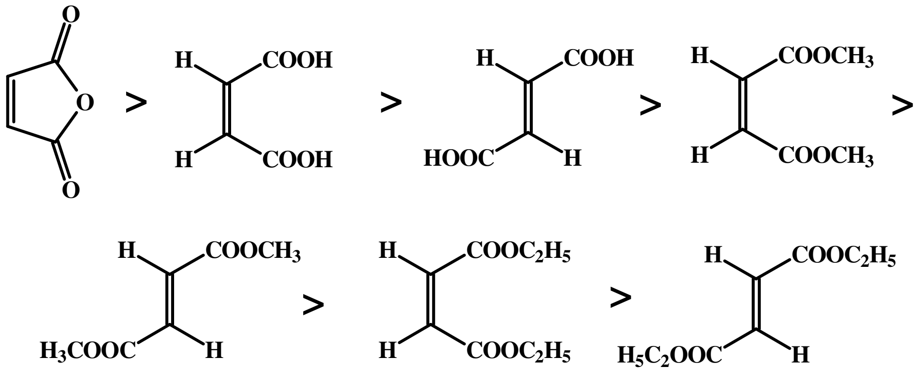
Effect of partial pressure of hydrogen: By varying the pressure of hydrogen in the range 103.5-106.3 KN m^{-2}, keeping the concentrations of other reactants constant. It was found that the rate of hydrogenation increased with increase in partial pressure. A plot of log V *versus* log $^{P}H_2$ gave a straight line with a unit slope indicating first order with respect to the partial pressure of hydrogen (Table-3).

Owing to the fragile nature of the hydrogenation system wide range of pressures could not be studied.

Effect of temperature: The rate of the reaction was found to increase with increase in temperature under other wise similar conditions. These results are in accordance with Arrhenius theory. (Table-4).

Product analysis: The ^{1}H NMR data of the olefins and their hydrogenated counterparts is presented in Table-7.

Effect of structure on the reactivity of substrate: The rate of hydrogenation of maleic anhydride, maleic acid, methyl maleate, ethyl maleate, fumaric acid, methyl fumarate and ethyl fumarate were found to be in the order:



The products obtained from the respective geometrical isomers are same. However, the *cis* alkenes are reduced by and large at a slightly higher rate than the *trans* alkenes. This could probably be due to the two larger substituents, which are located farther apart in *trans* isomers than in the *cis* isomers. Therefore, it could be reasonable to expect less crowding and less van der Waal's strain leading to a greater stability of *trans* isomers over *cis* isomers. In view of this, complexation of *cis* isomer with catalyst in the inner layers is relatively greater than the *trans* isomer. Thus *cis* compounds react faster than *trans* compounds.

According to the available literature reports and mechanisms, the olefin adsorbs on the surface of the catalyst and the hydrogen adsorbed on the catalyst is cleaved to hydrogen atoms and the addition takes place from the less hindered side[11].

Mechanism of hydrogenation: On the basis of foregoing discussion coupled with the kinetic results a plausible mechanism was proposed as shown in **Scheme-I**. Following are the important steps of the **Scheme-I**.

TABLE-3

EFFECT OF VARIATION OF PARTIAL PRESSURES OF HYDROGEN

Reaction conditions: 10^5 [substrate]: 0.75 mol dm^{-3}; 10^5 [Catalyst]: 0.40 mol dm^{-3}; Solvent: THF; Temperature: 288-306 K

10^5 [S] mol dm^{-3}	Maleic anhydride			Maleic acid			Fumaric acid			Methyl maleate			Methyl fumarate			Ethyl maleate			Ethyl fumarate		
	288K	300K	306K	288K	300K	306K	288K	300K	306K	288K	300K	306K	288K	300K	306K	288K	300K	306K	288K	300K	306K
1.035	6.06	6.86	7.09	4.89	5.25	5.41	4.32	4.58	4.80	4.09	4.22	4.41	3.94	4.21	4.30	2.10	2.57	2.80	2.06	2.49	2.69
1.045	6.12	6.93	7.16	4.94	5.30	5.46	4.37	4.62	4.85	4.13	4.26	4.45	3.98	4.25	4.34	2.12	2.60	2.82	2.08	2.51	2.72
1.050	6.15	6.96	7.19	4.96	5.32	5.49	4.39	4.65	4.87	4.15	4.28	4.47	4.00	4.28	4.36	2.13	2.61	2.84	2.09	2.53	2.73
1.055	6.18	7.00	7.22	4.98	5.35	5.52	4.41	4.67	4.90	4.17	4.30	4.49	4.01	4.29	4.38	2.14	2.62	2.85	2.10	2.54	2.75
1.060	6.21	7.03	7.26	5.01	5.37	5.44	4.43	4.70	4.92	4.19	4.32	4.51	4.05	4.31	4.40	2.15	2.64	2.86	2.11	2.55	2.76
1.063	6.23	7.05	7.28	5.02	5.39	5.56	4.44	4.71	4.94	4.20	4.34	4.53	4.06	4.32	4.42	2.16	2.65	2.87	2.12	2.56	2.77

TABLE-4

EFFECT OF TEMPERATURE

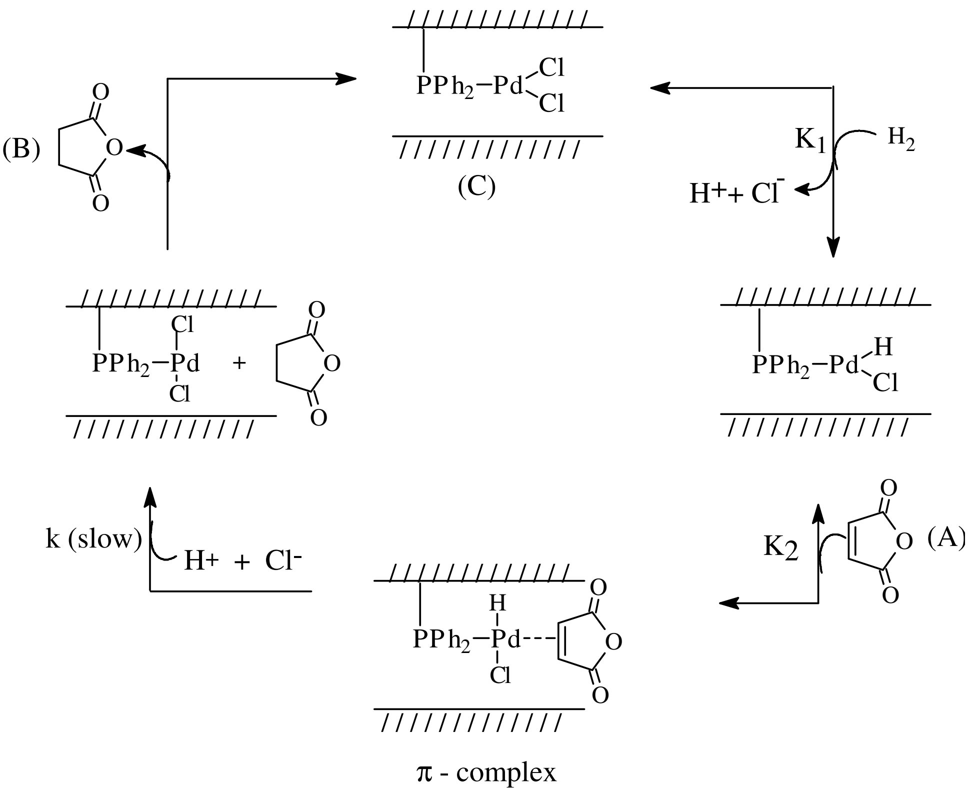
Reaction conditions: 10^5 [substrate]: 0.75 mol dm^{-3}; 10^5 [Catalyst]: 0.40 mol dm^{-3}; Solvent: THF; $^PH_2$: 1.063 × 10^2 KNm^{-2}

Temperature (K)	Maleic anhydride	Maleic acid	Fumaric acid	Methyl maleate	Methyl fumarate	Ethyl maleate	Ethyl fumarate
288	6.23	5.02	4.84	4.20	4.05	2.16	2.12
294	6.62	5.20	4.87	4.28	4.19	2.40	2.34
300	7.05	5.39	4.90	4.34	4.32	2.65	2.56
306	7.28	5.56	4.94	4.53	4.42	2.87	2.77

TABLE-5

ACTIVATION PARAMETERS AND THERMODYNAMIC PARAMETERS INVOLVING K_1 AND K_2

Olefins	Activation parameters			Thermodynamic parameters involving K_1 and K_2					
	10^{-4} k_{306}	$\Delta H^{\#}$ kJ mol^{-1}	$-\Delta S^{\#}$ J mol^{-1} K^{-1}	K_1	$-\Delta H_1$ kJ mol^{-1}	$-\Delta S_1$ J $mol^{-1}K^{-1}$	K_2	$-\Delta H_2$ kJ m ol^{-1}	$-\Delta S_2$ J $mol^{-1}K^{-1}$
Maleic anhydride	3.87	18.4	116	99.6	11.9	8.64	225	22.9	30.0
Maleic acid	3.56	23.1	101	94.7	20.1	27.8	156	18.8	19.5
Fumaric acid	3.02	27.4	89.1	100	25.2	44.1	156	17.9	16.4
Methyl maleate	3.93	31.1	74.9	62.1	29.3	61.3	163	17.1	13.6
Methyl fumarate	3.55	25.4	94.1	63.8	22.1	37.8	190	18.5	16.9
Ethyl maleate	2.52	42.8	40.2	73.6	28.9	58.7	121	26.6	47.1
Ethyl fumarate	2.79	47.9	22.4	63.1	31.9	68.8	113	19.6	24.6



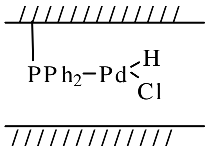
A = Maleic anhydride , B = Succinic anhydride,
C = The anchored montmorillonite diphenyl phosphino palladium(II) chloride
Scheme-I: Mechanism for hydrogenation of maleic anhydride to succinic anhydride

$$C + H_2 \overset{K_1}{\rightleftharpoons} C_1$$

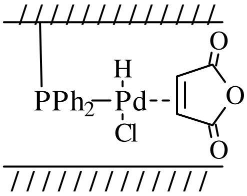
$$C_1 + S \overset{K_2}{\rightleftharpoons} C_2$$

$$C_2 \xrightarrow[\text{Slow}]{k} P + C$$

where C is the catalyst employed in the reaction, C_1 is the intermediate complex formed between Pd(II) and hydrogen whose structure is,



C_2 is a π-complex species formed in the second equilibrium step having the structure



'S' is the substrate and 'P' is the hydrogenated product of the substrate.

Thus, rate of the reaction for **Scheme-I** comes out as given in the following rate expression,

$$V = \frac{k K_1 K_2 [C] [H_2] [S]}{1 + K_1 [C] + K_2 [S] + K_1 K_2 [C] [S]}$$

Rearranging the above equation we get

$$k' = \frac{V}{[H_2]} = \frac{k K_1 K_2 [C] [S]}{1 + K_1 [C] + K_2 [S] + K_1 K_2 [C] [S]}$$

Taking reciprocals of the above equation

$$\frac{1}{k'} = \frac{1}{k K_1 K_2 [C] [S]} + \frac{1}{K K_2 [S]} + \frac{1}{k K_1 [C]} + \frac{1}{k}$$

Least square plot of 1/k *versus* 1/[S] at a known catalyst concentration gave a straight line with a positive slope and intercept. These observations are thus keeping in with the proposed mechanism.

$$\text{Slope} = \frac{1}{k K_1 K_2 [C]} + \frac{1}{k K_2}$$

and $$\text{intercept} = \frac{1}{kK_1[C]} + \frac{1}{k}$$

The ratio of intercept to slope gave K_2, which was determined at different temperature from which ΔH has been calculated. The free energy values related to K_2 were obtained from Van Hoff's reaction isotherm *i.e.*

$$\Delta G = -RT \ln K_2$$

And ΔS was calculated from Gibbs-Helmholtz equation according to literature procedures.

$$\Delta G = \Delta H - T\Delta S$$

Similarly the least square plot of 1/k' *versus* 1/[C] at constant substrate concentration gave a straight line with a positive slope and intercept. From the ratio of intercept and slope K_1 was evaluated. The corresponding thermodynamic parameters have been calculated and presented (Table-5). The obtained ΔG values were all negative indicating the feasible formation of the complex C_2. Negative entropy values probably indicate that C_1 and C_2 are structurally organized. Substitution of the values of K_1 and K_2 in the slopes or intercepts of above plots the rate constant of the slow step k was evaluated at different temperatures. The corresponding activation parameters have been calculated (Table-5). According to the available literature reports and mechanisms, the olefin adsorbs on the surface of the catalyst and the hydrogen adsorbed on the catalyst is cleaved to hydrogen atoms and the addition takes place from the less hindered side[10-13]. The negative values of ΔG_1 and ΔG_2 indicate the spontaneity of the formation of C_1 and C_2 species given in **Scheme-I**. It is also interesting to note that ΔS_1 and ΔS_2 values are also negative indicating reorganization of coordination spheres during the formation of C_1 and C_2 species, respectively. However, nothing much could be interpreted quantitatively owing to an irregular trend when an alkyl group replaces hydrogen in a *cis* isomer or *trans* isomer. In any case the entropy of activation values are negative for all the substrates showing changes in the coordination spheres of catalyst before yielding the end product. Isokinetic temperature (β) value calculated from Exner's theory came out as 312 K, which is agreeing well with that of Leffler's approach (316 K) (Table-6). It appears that both entropy and enthalpy factors are important in controlling the rate of hydrogenation as the β value is close to the experimental temperature range (288-306 K) of the present study.

TABLE-6
STRUCTURE REACTIVITY PARAMETERS

Entry	Type of plot	Slope	Correlation co-efficient (γ)
A	Exner log k (300) *versus* log k (306)	Slope = 0.523, β = 312	0.795
B	Leffler $\Delta H^{\#}$ *versus* $\Delta S^{\#}$	Slope = 0.316	0.999
C	Taft's log k *versus* σ^* (for *cis* olefins)	Slope = 0.475	0.704
D	Taft's log k *versus* E_s(for *cis* olefins)	slope = 0.169	0.869
E	Taft's log k *versus* σ^* (for *trans* olefins)	slope = 0.080	0.079
F	Taft's log k *versus* E_s(for *trans* olefins)	slope = 0.040	0.223

TABLE-7
^{1}H NMR DATA OF SUBSTRATES AND PRODUCTS

Substrate	NMR	Product	NMR
Maleic anhydride	δ 7.1 (s, =CH-, 2H)	Succinic anhydride	δ 3.0 (s, -CH$_2$-, 4H)
Maleic acid	δ 6.3 (s, =CH-,2H), 9.95 (s, -COOH, 2H),	Succinic acid	δ 2.5 (s, -CH$_2$-, 4H), δ 9.89 (s, -COOH, 2H).
Fumaric acid	δ 6.7 (s, =CH-, 2H), δ 9.9 (s, -COOH, 2H)	dimethyl succinate	δ 2.51 (s, -CH$_2$-, 4H), δ 3.61 (s, -OCH$_3$, 6H).
Methyl maleate	δ 6.32 (s, =CH-, 2H), δ 3.88 (s, -OCH$_3$, 6H).		
Methyl fumarate	d 6.72 (s, =CH-, 2H), δ 3.78 (s, -OCH$_3$, 6H).	Diethyl succinate	δ 2.50 (s, -CH$_2$-, 4H), δ 3.89 (q, -CH$_2$-, 4H) δ 1.31 (t, -CH$_3$, 6H)
Ethyl maleate	δ 6.37 (s, =CH, 2H), δ 2.25 (q, -CH$_2$, 4H), δ 1.31 (t, -CH$_3$, 6H)		

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