

Effects of solvents polarity parameters on heterogeneous catalytic hydrogenation of cyclohexene in molecular solvents

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ABSTRACT

Heterogeneous catalytic hydrogenation of cyclohexene, catalyzed by Pt/Al₂O₃, was carried out in thirteen various solvents (four alcoholic solvents, six aprotic polar solvents and three non polar solvents) at 25 °C. Single-parameter correlations of log k vs. normalized polarity parameter (E_T^N), hydrogen-bond acceptor basicity (β), hydrogen-bond donor acidity (α) and dipolarity/polarizability (π^*) do not give acceptable results. In addition, log k does not show an acceptable dual-parameter correlation with E_T^N and α , E_T^N and β , E_T^N and π^* , α and β , α and π^* and β and π^* . Like that, three parameter and four parameter correlations of log k vs. solvatochromic parameters don't give acceptable results. Correlations of log k vs. acceptor number (AN), donor number (DN), relative static permittivity (ϵ) and dipole moment (μ) are tested but don't give reasonable results. However in case of alcoholic solvents, reaction rate constants increase with increasing of hydrogen-bond donor acidity (α), dipolarity/polarizability (π^*), normalized polarity parameter (E_T^N), relative static permittivity (ϵ), dipole moment (μ) and acceptor number (AN) and decrease with increasing of hydrogen-bond acceptor basicity (β) and donor number (DN). These effects are attributed to the non-polar nature of the reactant and competitive adsorption of solvent on catalyst surface.

Keywords: Heterogeneous catalytic hydrogenation; Solvatochromic parameters; Solvent effects

INTRODUCTION

Catalytic hydrogenation is one of the most useful, versatile, and environmentally acceptable reaction routes available for organic synthesis. This reaction is usually carried out in a liquid-phase using batch type slurry processes and a supported noble metal (Pd, Pt, Ni or Rh) catalyst [1–4]. The performance of noble metal catalysts in liquid-phase hydrogenation has been found to be dependent on several factors such as liquid composition (substrate structure, solvent effect, etc.), catalyst nature (active sites composition and morphology, support effect, modifiers, etc.), and reaction conditions (temperature, pressure, etc.) [5]. The solvent can play multiple roles in hydrogenation reactions such as dissolving reactants and products, controlling the reaction rate and the exothermicity of the reactions.

In addition, specific solvent-solute interactions can favor a higher rate and/or selectivity [6-10]. The applications of heterogeneous catalysts have been increased dramatically because of their simple regeneration and easy separation from the organic media. These can facilitate the use of continuous processes and the development of environmental friendly plants [10, 11]. For a heterogeneously catalyzed system, the solvent can also help to maintain a clean catalyst surface by removing the poisons or inhibitors [7].

A limited number of studies have dealt quantitatively with the kinetic aspects of solvent effects on a heterogeneous catalyst [12-14]. For example, the nature of the solvent can be useful

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in determining the reactive functional group for a selective hydrogenation from the substrate mixtures [15].

Solvent effects on heterogeneous catalysis have been rationalized by correlating reaction rates and product distributions with the solvent polarity or its dielectric constant [16-19]. There is no doubt that such solvent properties can influence the reaction kinetics. More work has to be done to achieve better understanding and quantitatively characterizing of these effects. These effects are, in fact, even more complicated with supported metal catalyst due to the possible interaction between the solvent and support [20-22].

We focused on the effect of the room temperature ionic liquid (RTIL) on the activity and selectivity of C=C and C=O hydrogenation in alcoholic solvents at 25 °C (use of acetone hydrogenation to propan-2-ol and cyclohexene hydrogenation to cyclohexane as model reactions) [23-24]. In addition, we saw that the $\log k_{\text{obs}}$ (observed rate constant) was correlated with π^* (dipolarity/polarizability) of the solvent mixture and the rate constant increases continuously with increasing the π^* . In this study, we focused on the effects of molecular solvents in catalytic hydrogenation of cyclohexene at 13 various solvents. We choose both polar and non-polar solvents as reaction media. Finally we try to achieve a relationship between $\log k_{\text{obs}}$ and solvent polarity parameters (such as hydrogen-bond donor acidity (α), hydrogen-bond acceptor basicity (β), dipolarity/polarizability (π^*), normalized polarity parameter (E_T^N), relative static permittivity (ϵ), dipole moment (μ), donor number (DN) and acceptor number (AN)) for the solvents used in this study.

EXPERIMENTAL

Materials

Methanol, ethanol, propan-1-ol, dimethyl sulfoxide (DMSO), triethylamine, carbon tetrachloride, benzene, acetonitrile, chloroform, methyl acetate, nitromethane, undecane, platinum dichloride, hydrochloric acid, 4-nitroanisole and 4-nitroaniline were obtained from Merck, propan-2-ol and alumina were obtained from Fluka. 2,6-Diphenyl-4-(2,4,6-triphenyl-1-pyridino)-phenolate, the indicator solute for the $E_T(30)$ scale was purchased from Aldrich. The chemical was of the highest purity

available and purified according to the literature[25].

Solvatochromic parameters measurements

Spectral measurements for determination of Solvatochromic parameters were taken by a Cinda 40 spectrophotometer. Temperature was controlled to 25 ± 0.1 °C by circulating water through NESLAB thermostat. Maximum absorption was determined from first derivative of wavelength scan. To check the reproducibility, the position of the maximum absorption in a particular solvent was repeated several times. The precision of replicated measurements were ± 1 nm. The concentrations of the probes in the solutions were 10^{-5} M, 10^{-6} M and 10^{-4} M for 4-nitroanisole, 4-nitroaniline and Reichardt's dye respectively.

Catalyst preparation

Pt/Al₂O₃ catalyst was prepared impregnating alumina with excess liquid. The impregnation solution was prepared by dissolving 500 mg PtCl₂ in 30 mL deionized water and 10 mL HCl (32%w/v). Then 5 g of γ -alumina was added to the impregnation solution and stirred for 30 minutes. The impregnated solid was separated by decantation of the solution, and dried at 100 °C for 12 hours. The catalyst was reduced in hydrogen flow (120 ml/min) at 400 °C for 1 hour and was characterized with XRD and BET methods.

Catalyst characterization Methods

Specific area and porosity were obtained from nitrogen adsorption-desorption isotherms at 77K performed in an automatic Quantachrom apparatus (Model Quantasorb) with Belsorp adsorption/desorption data analysis software in the 0.05 to 0.995 relative pressure ranges. BET surface area was calculated from a linear part of the BET plot according to IUPAC recommendations. Pore size distributions were calculated from the N₂ adsorption branch using the Horvath-Kawazoe model. Mean pore diameter and total pore volume ($P/P_0=0.99$) were calculated from BET plot by Belsorp adsorption/desorption data analysis software.

XRD of the catalyst was carried out from 4° to 70° (2 θ) using a Bruker D4 X-ray diffractometer operating at 40kV and 30mA with Cu K α radiation ($\lambda=1.542\text{\AA}$) and a Ni filter.

Counts were accumulated every 0.02 (2θ) at a scan speed of 1° ($2\theta/\text{min.}$) in 25°C .

Catalytic run

In a typical run, a solution of cyclohexene in solvent (0.2 g cyclohexene in 20 mL solvent) was added to 50 ml three-necked flask attached to a thermometer, a condenser and a hydrotreater (including a hydrogen cylinder, hydrogen flowmeter and valves). After replacing the air in the flask completely with hydrogen, 0.02g of alumina supported platinum was added. The reaction mixture was stirred vigorously with a magnetic stirrer (1250rpm) and was kept at desired temperature (25°C). During the reaction, 1 μl of reaction mixture was taken and injected to the HP6890 gas chromatograph with 60 m HP5 column.

RESULTS AND DISCUSSIONS

Catalyst characterization

The presented experimental data indicate that reactions such as an alkene hydrogenation take place on single active atom sites on the metal surface. The various surface atoms differ in their coordinative unsaturation, as a result it is reasonable to expect different hydrogenation rates as well as differing degrees of interaction with solvent molecules.

The sample reduced at 400°C exhibits the fcc XRD pattern with peaks at $2\theta=39.8$, 46.3 and 67.3. The average crystallite size, L of the particle was determined by XRD line broadening technique using Scherrer equation, $L=0.94\lambda/b.\cos\theta$; in which λ is the wavelength of X-ray and b is the relative peak broadening. The crystallite size of Pt particles was obtained to be 5.8 nm.

The mean diameter of pores obtained from BET plot and pore size distribution was 8.05nm and 2.45nm respectively. The BET surface area and the total pore volume ($P/P_0=0.990$) of the supported Pt catalyst was $373.7\text{m}^2\text{g}^{-1}$ and $0.7519\text{cm}^3/\text{g}$ respectively.

Solvatochromic parameters effects on the reaction kinetics

The first-order rate constants of the reaction in each solvent were obtained at 25°C . The reaction rate constants were calculated by plotting the logarithm of concentration of cyclohexene vs. time and are summarized in Table 1. The solvatochromic parameters for all solvents have been determined in our laboratory (Table 1). In addition, Table 1 has the relative static permittivity (ϵ), dipole moment (μ), donor number (DN) and acceptor number (AN) for the solvents used in this study.

Table 1. First-order rate constant of the reaction in the various solvents along with the polarity and solvatochromic parameters of media

Solvent	$k_{\text{obs}} \times 10^2$ ($\text{s}^{-1}\text{g}^{-1}$)	E_T^N	π^*	β	α	DN(kcal/mol)	AN	ϵ	μ
methanol	1.39	0.76	0.57	0.81	1.16	19.1	41.3	33	1.7
ethanol	1.29	0.65	0.51	0.91	0.97	19.2	37.1	24.3	1.69
1-propanol	1.09	0.62	0.56	0.94	0.87	19.8	37.7	20.1	1.68
2-propanol	1.03	0.54	0.49	1.07	0.74	21.1	33.8	18.3	1.66
DMSO	1.92	0.44	1	0.76	0	29.8	19.3	47.2	3.96
triethylamine	0.48	0.043	0.14	0.71	0	61	1.2	3.2	4.12
acetonitrile	1.13	0.46	0.75	0.31	0.19	14.1	19	35.97	3.92
Chloroform	No reaction	0.259	0.58	0	0.44	7.5	23.1	4.81	1.01
methylacetate	3.01	0.29	0.6	0.42	0	16.5	10.7	6.74	1.72
nitromethane	1.10	0.48	0.85	0	0.22	2.7	20.5	36.48	3.56
Carbon tetraChloride	0.17	0.052	0.28	0	0	0	8.6	2.24	0
benzene	1.18	0.111	0.59	0.1	0	20	8.2	2.28	0
undecane	0.19	0.009	0	0	0	0	0	2	0

The table 1 shows that three types of solvents are used in this study; four alcoholic solvents, six aprotic polar solvents and three non-polar solvents. The alcoholic solvents are homologous and differ from each other only in one CH₂ group. The aprotic solvents have six various polar groups and the non-polar solvents include a saturated hydrocarbon, an aromatic hydrocarbon and a chlorinated compound.

We saw in our previous work that logarithm of observed rate constant correlate satisfactorily with solvatochromic parameters [23-24]. Thus, as first step, we examine the correlation of logarithm of observed rate constant with solvatochromic parameters for cyclohexene hydrogenation in these 13 various solvents.

Single-parameter correlations of log k vs. E_T^N do not give acceptable results in the solutions ($r = 0.630$ and $F=6.570$ (F is statistical Fisher number)). The non acceptable correlation of log k vs. E_T^N is not unexpected (Figure 1), because these two parameters doesn't vary in a same way. Normalized polarity parameter is blend of π^* (dipolarity/ polarizability) and α (hydrogen-bond donor acidity) of the media. Therefore, correlations of log k vs. π^* and α in the solutions were considered.

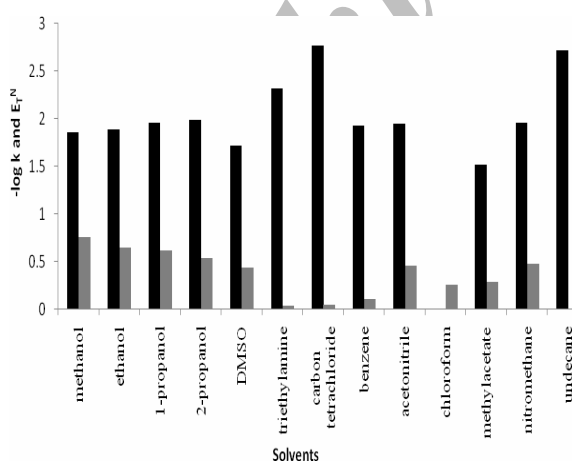


Fig. 1. Variation of $-\log k$ (black lines) and E_T^N (gray lines) for various alcoholic, polar aprotic and non-polar solvents used in this study.

As discussed for E_T^N , in a same manner, correlation of log k vs. α and π^* don't give acceptable results (for correlation of log k with α $r=0.288$ and $F=0.902$ and for correlation of log k

with π^* $r=0.771$ and $F=14.701$). For hydrogen bond donor basicity, β , $r=0.456$ and $F=2.628$. As seen from these results, single parameter correlation of log k with solvatochromic parameters doesn't give acceptable results and we must examine more complex models.

Dual parameter correlation of log k vs. E_T^N and α , E_T^N and β , E_T^N and π^* , α and β , α and π^* and β and π^* were considered. The results were better than single parameter correlations but are not acceptable. (for correlation of log k vs. E_T^N and α , $r=0.780$ and $F=6.993$, for correlation of log k vs. E_T^N and β , $r=0.633$ and $F=3.004$, for correlation of log k vs. E_T^N and π^* , $r=0.803$ and $F=8.156$, for correlation of log k vs. α and β , $r=0.458$ and $F=1.193$, for correlation of log k vs. α and π^* , $r=0.800$ and $F=7.979$ and for correlation of log k vs. β and π^* , $r=0.844$ and $F=11.170$).

Three parameters correlation of log k vs. E_T^N and α and β , E_T^N and α and π^* , E_T^N and β and π^* , α and β and π^* were considered and do not give acceptable results. (for correlation of log k vs. E_T^N and α and β , $r=0.815$ and $F=5.281$, for correlation of log k vs. E_T^N and α and π^* , $r=0.803$ and $F=4.846$, for correlation of log k vs. E_T^N and β and π^* , $r=0.845$ and $F=6.639$ and for correlation of log k vs. α and β and π^* , $r=0.845$ and $F=6.659$).

Finally we try to correlate log k with all four solvatochromic parameters and as a result we saw that $r=0.889$ and $F=0.937$. Because these 13 solvents are three different types, correlations of log k with solvatochromic parameters don't give acceptable results. Thus we separate these three types of solvents and try to correlate log k vs. solvatochromic parameters for each type of solvents separately.

In this study we use only four alcoholic solvents, thus we can't use statistical methods in this case. Figure 2 shows that log k in alcoholic solvents increases with increasing of E_T^N , α and π^* and decreases with increasing of β . In the liquid phase reactions, an increase in solvent polarity results in an increase in the rates of certain reactions in which the charge density is greater in the activated complex than the reactants. In heterogeneous catalytic hydrogenation, the reaction occurs in the surface of the catalyst (far from bulk of solvent). Then the solvent can not directly affect the energetic

level and the activated complex of the reactants. Polar solvents increase the adsorption of non-polar substrates on the catalyst while non-polar solvents facilitate the adsorption of polar species. It seems that with increasing polarity (E_T^N , α and π^*) of the media, the tendency of the reactants increases on the catalyst surface and for this reason the reaction rate increases. In case of β parameter, increasing basicity of solvent can increase the competitive adsorption of solvent on the catalyst and then decrease the adsorption of cyclohexene and reaction rate.

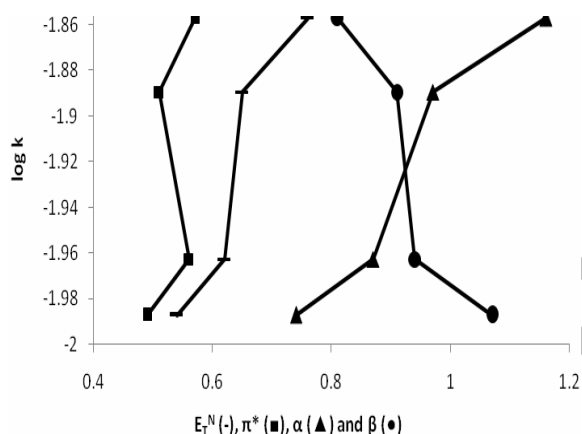


Fig. 2. Variation of log k vs. E_T^N (-), π^* (■), α (▲) and β (●) for alcoholic solvents

Fig. 3 shows the variation of log k vs. E_T^N , α , β and π^* . There is no reasonable relevance between rate constant and solvatochromic parameters for polar aprotic solvents. In this case, we can not establish any correlation between log k and solvatochromic parameters. In fact, because of this chaotic behavior of rate constants of hydrogenation of cyclohexene in aprotic solvents, we can not extract good correlation between log k and solvatochromic parameters for all solvents.

Last type of solvents we used in this study is three non polar solvents. Table 1 shows that variation of log k vs. solvatochromic parameters for this type of solvents is close to polar aprotic solvents. Thus we can not see any reasonable relationship between log k and solvatochromic parameters. In fact, only alcoholic solvents show good correlation between log k and solvatochromic parameters.

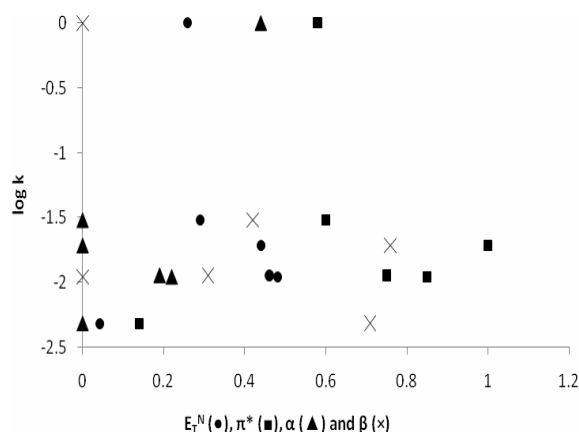
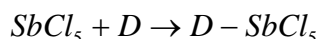


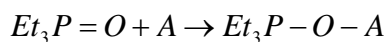
Fig. 3. Variation of log k vs. E_T^N (●), π^* (■), α (▲) and β (x) for aprotic polar solvents.

Donor and Acceptor number effects on the reaction rate

An empirical semiquantitative measure of the nucleophilic properties of electron pair donor solvents is provided by the donor number DN (or donicity) of Gutmann [26, 27]. This donor number has been defined as the negative ΔH values for 1:1 adduct formation between antimony pentachloride and electron-pair donor solvents (D) in dilute solution in the non-coordinating solvent 1,2-dichloroethane:



An analogous empirical quantity for characterizing the electrophilic properties of electron pair acceptor solvents has been derived by Gutmann and coworkers from the ^{31}P NMR chemical shifts produced by the electrophilic actions of acceptor solvents A in triethylphosphane oxide:



$$AN = \frac{\delta_{corr}(A) - \delta_{corr}(n-C_6H_{14})}{\delta_{corr}(Et_3PO - SbCl_5) - \delta_{corr}(n-C_6H_{14})} \times 100 = \Delta\delta_{corr} \times 2348 / ppm$$

These quantities have been termed acceptor number AN (or acceptivity) and they were obtained from the relative ^{31}P NMR chemical shift values δ_{corr} (n-hexane as reference solvent) with respect to that of the 1:1 adduct $Et_3PO - SbCl_5$ dissolved in 1,2-dichloroethane, which

has been arbitrarily taken to have the value of 100. The acceptor numbers are dimensionless numbers expressing the acceptor property of a given solvent relative to those of SbCl_5 , which is also the reference compound for assessing the donor numbers.

We try to derive an equation for $\log k$ vs. acceptor and donor numbers of solvents. Single parameter correlation of $\log k$ vs. AN and DN don't give acceptable results for solvents used in this study. For correlation of $\log k$ with AN, $r=0.490$ and $F=2.837$ and for correlation of $\log k$ with DN, $r=0.236$ and $F=0.592$. In addition, dual parameter correlation of $\log k$ vs. AN and DN were tested and didn't give reasonable results like single parameter correlations. ($r=0.561$ and $F=1.838$)

Tab. 1 shows that variation of $\log k$ vs. AN and DN are regular only in case of alcoholic solvents. For polar aprotic and non polar solvents, we can not see any reasonable relationship between $\log k$ and AN or DN. Increasing donor number of solvents show the Lewis base ability of the solvents. Thus, in alcoholic solvents, increasing of DN can increase the competitive adsorption of solvent on the catalyst and then decrease the adsorption of cyclohexene and reaction rate. Vice versa, addition of AN shows the addition of Lewis acid properties of solvents. Thus, in case of alcoholic solvents, addition of AN decrease the competitive adsorption of solvent on the catalyst and then increase the reaction rate constant of hydrogenation of cyclohexene on Pt.

Relative static permittivity and dipole moment effects on the reaction rate

Fig. 4 shows the variation of $\log k$ vs. relative static permittivity, ϵ , of the solvents. It is obvious from figure 4 that only for alcoholic solvents, logarithm of rate constant increase with increasing of ϵ . But for other solvents, there are no reasonable relationship between $\log k$ and ϵ . Like ϵ , in case of dipole moment, μ , one can see from table 1 that only alcohols obey from clear relationship and rate constant of hydrogenation of cyclohexene in alcohols increase with increasing of μ .

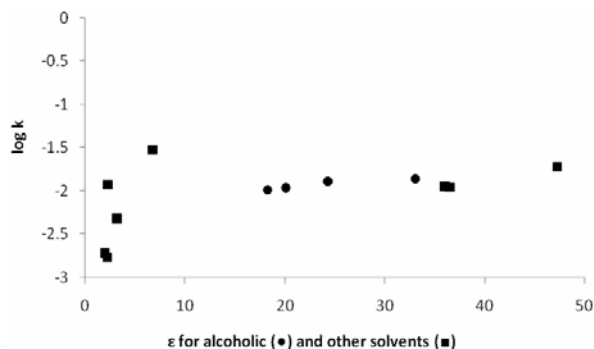


Fig. 4: Variation of $\log k$ vs. ϵ for alcoholic (●) and other solvents (■) used in this study.

CONCLUSION

The reaction rate constant of a catalytic hydrogenation reaction in thirteen various solvents were obtained at 25 °C. As we saw, there is no reasonable relationship between reaction rate constants and hydrogen-bond donor acidity (α), hydrogen-bond acceptor basicity (β), dipolarity/polarizability (π^*), normalized polarity parameter (E_T^N), relative static permittivity (ϵ), dipole moment (μ), donor number (DN) and acceptor number (AN) for polar aprotic and non polar solvents. But the reaction rate constants increase with increasing of the α , π^* , E_T^N , ϵ , μ and AN and decrease with increasing of DN and β in alcoholic solvents. As one of the possible explanations about this phenomenon, it was demonstrated that α , π^* , E_T^N , ϵ , μ and AN of the media have an important role in determining solvent effects on the reaction rate constants. This was attributed to the non-polar nature of the cyclohexene. The reactant tendency to the catalyst surface increases by increasing the α , π^* , E_T^N , ϵ , μ and AN and thus the reaction rate increases. Furthermore, increasing DN and β of solvents indicate the Lewis base ability of the solvents. Thus, in alcoholic solvents, increasing of DN and β of solvent can increase the competitive adsorption of solvent on the catalyst and then decrease the adsorption of cyclohexene and reaction rate.

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