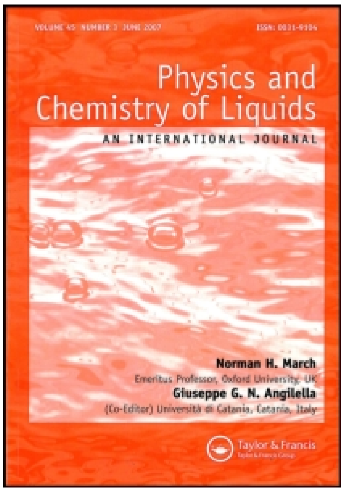

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Hydrolysis of Sucrose by Heterogeneous Catalysis

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HYDROLYSIS OF SUCROSE BY HETEROGENEOUS CATALYSIS

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The reaction kinetics of the hydrolysis of sucrose by solid catalysts was investigated using polarimetry. Silica included heteropoly acid was used as a catalyst. At the optimizing conditions the activation parameters have been evaluated using the Arrhenius and Eyring plots.

Keywords: Hydrolysis; Sucrose; Heterogeneous catalysis

1. INTRODUCTION

The hydrolysis of sucrose by homogeneous acid catalyst has been of central importance in the development of the subject of chemical kinetics [1–4]. Recently hydrolysis of sucrose by heterogeneous catalysts are also paid attention [5–8]. Any insoluble form of a heterogeneous catalysts has several advantages, over liquid acid systems: decreased corrosion, safe catalyst handling, easier catalyst recycle and quicker catalyst regeneration. In this article the aim is to investigate the hydrolysis of sucrose by heterogeneous acid catalysis, using silica included 12-tungstophosphoric acid. Thermodynamic and kinetic parameters are also reported.

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2. EXPERIMENTAL

Sucrose, tetraethyl ortosilicate, tungstophosphric acid and 1-butanol were of analytical grade Merck, and were used as received. Water was double distilled and degassed before use. Silica included 12-tungstophosphoric acid catalyst was prepared by the earlier method [9]. Hydrolysis of sucrose was investigated in the temperature interval of 60 to 85°C with 3, 5 and 7 g catalyst in 250 ml stirred solution of 0.3 M sucrose. Portions of the solution after centrifuge were taken out at known time intervals and the rotation of polarized light was noted with the help of a Polax-D type polarimeter.

3. RESULT AND DISCUSSION

3.1. Inversion of Sucrose

The hydrolysis of sucrose to glucose and fructose, using the acid catalyst, proceeds according to the well-known equation:

$$\underset{\text{[surcrose]}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow{H^+} \underset{\text{[glucose]}}{C_6H_{12}O_6} + \underset{\text{[fructose]}}{C_6H_{12}O_6} \tag{1}$$

The reaction is irreversible and first-order with respect to the concentration of sucrose. Hydrolysis of sucrose by heterogeneous catalysis needs an insoluble solid acid. Recently solid acid catalysts such as zeolites [5, 8], polymers [6], resin [7] were employed for hydrolysis of sucrose. For this reaction we used some transition metal oxides (Nb_2O_5, Al_2O_3 and V_2O_5/Al_2O_3) and found V_2O_5/Al_2O_3 as a reactive catalyst [10]. In this work we used a new insoluble catalyst, silica included 12-tungstophosphoric acid [9], for hydrolysis of sucrose. The progress of hydrolysis of sucrose was followed by the angles of rotation r_t of the various sugar solutions at different temperatures with time (min) and as typical the results at 60°C are presented graphically in Figure 1.

The reaction exhibit a first-order dependence with the following rate law

$$R = kC_{\text{suc.}}m_{\text{cat.}}^{n} \tag{2}$$

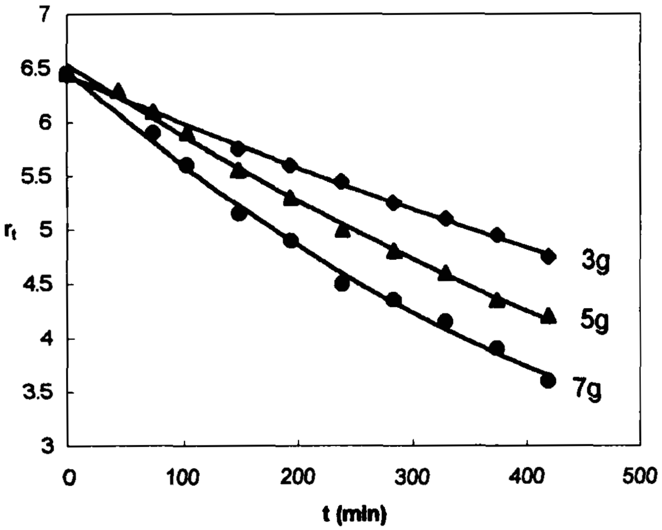

FIGURE 1 Variation of angles of rotation *vs.* time at 333 K.

Here k is the rate constant, m is catalyst concentration ($g \cdot lit^{-1}$) and n is reaction order of catalyst.

As the catalyst concentration is always constant at each experiment, so the rate law will be as follows:

$$R = k'C_{suc} \tag{3}$$

where

$$k' = km^{n}_{cat} \tag{4}$$

or

$$\ln k' = \ln k + n \ln m_{cat} \tag{5}$$

By knowing r_t we can determine the value of k' using the following equation

$$[\ln(r_{\infty} - r_t)/(r_{\infty} - r_o)] = -k't \tag{6}$$

The value of $r_{\infty} = -2.8$ was calculated by the Guggenheim method [11, 12] with data for 3 g of catalyst at 60°C. It is clear that the plots of $\ln[(r_{\infty} - r_t)/(r_{\infty} - r_o)]$ *vs.* t(min) should be linear. Such plots were obtained in the present study and from the slope the value of k' was evaluated. As a typical for 3 g catalyst 60°C, results are presented in Figure 2. The linearity shown in Figure 2 supported a first-order dependence on sucrose. The plots of ln k' *vs.* ln m_{cat}(Eq. (5)) should be linear with a slope of n and, from the intercept, the values of the rate constant k at different temperatures were obtained, the values being reported in Table I. One can write the following Arrhenius equation

$$k = A\exp(-E_a/RT) \tag{7}$$

and as such a plot of ln k *vs.* $1/T$ will give a straight line. From the slope and intercept of this plot, the activation energy (E_a) and

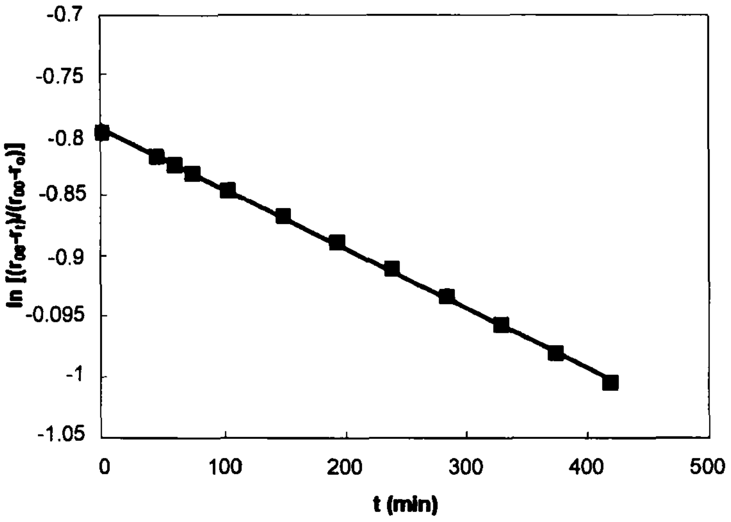

FIGURE 2 Variation of ln $[(r_\infty - r_t)/(r_\infty - r_o)]$ *vs.* time for 3 g of catalyst at 333 K.

TABLE I Rate constants for hydrolysis of sucrose by silica included 12-tungstophosphoric acid at different temperatures

Temperature		*Rate constant*			
(*K*)	$(1/T) \times 10^4$	$(k \times 10^6 s^{-1})$	$(k/T) \times 10^9$	*lnk*	*ln*(k/T)
333	30.03	1.49	4.47	−13.42	−19.22
343	29.15	2.31	6.73	−12.98	−18.82
353	28.32	6.15	17.42	−11.99	−17.85
358	27.93	11.10	31.00	−11.48	−17.29

frequency factor (*A*) may be calculated, respectively. Results are given in Table II and also displayed graphically in Figure 3.

The Eyring equation [13] may be suitably applied in the following form:

$$k = \frac{RT}{Nh}\exp(T\Delta S^{\neq} - \Delta H^{\neq})/RT \tag{8}$$

where *k* is the rate constant and the other symbols have their usual significance. The equation leads to

$$\ln(k/T) = \ln(R/Nh) + \Delta S^{\neq}/R - \Delta H^{\neq}/RT \tag{9}$$

TABLE II Activation parameters for hydrolysis of sucrose by silica included 12-tungstophosphoric acid

$\Delta H^{\neq}$ (*kJ/mol*)	$\Delta S^{\neq}$ (*kJ/mol · K*)	E_a (*kJ/mol*)	$A \times 10^{-6}$
77.29	−0.127	80.18	4.72

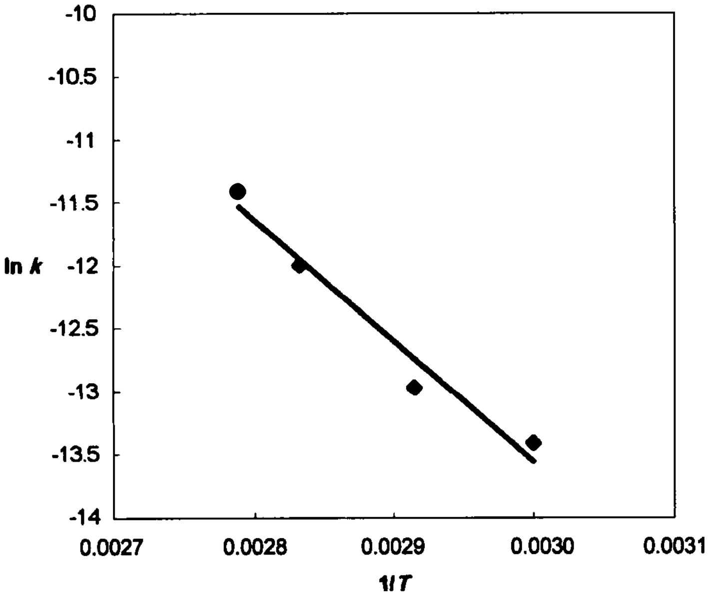

FIGURE 3 Arrhenius plot ln *k* vs. 1/*T*.

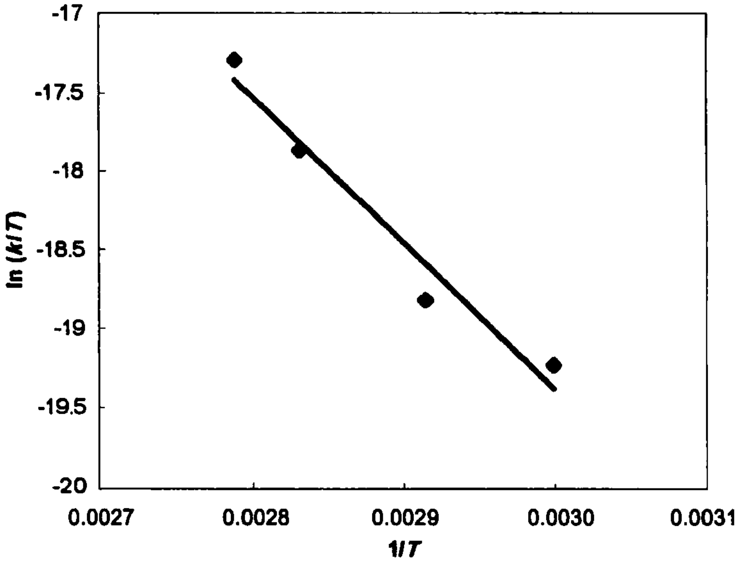

FIGURE 4 Plot of Eyring $\ln(k/T)$ *vs.* $1/T$.

Thus a plot of ln (k/T) *vs.* $1/T$ should give a straight line, the slope and intercept of which may be used to compute enthalpy of activation, $\Delta H^{\neq}$ and entropy of activation. $\Delta S^{\neq}$ values, respectively. The values obtained are also reported in Table II and displayed in Figure 4.

4. CONCLUSION

For achieving hydrolysis is not to be feasible for such reaction, the following equation has recently been given by Bond [14]:

$$E_{\text{app}} = E_{\text{true}} - \Delta H_{\text{A}} + \Delta H_{\text{B}} \qquad (10)$$

The above equation refers for a binary system in which one of the components, A makes a strong bond with the surface $\Delta H \ll 0$. Hence, we suggest that for hydrolysis of sucrose one may select a suitable catalyst in which the magnitude of ΔH_{ads} for H_2O should not be so high, which may be evaluated by theoretical or experimental methods. So that in spite of Al_2O_3 and Nb_2O_5 which are hydrophilic catalysts

[10] the silica included 12-tungstophosphoric acid has less tendency to the adsorption of water, and therefore could hydrolysis sucrose. The advantages of this catalyst are simplicity of production, insolubility in water and high reactivity for hydrolysis.

Acknowledgments

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