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Liquid Phase Catalytic Hydrogenation of Acetone

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The hydrogenation of acetone in various solvents on Raney nickel was studied at different temperatures and concentrations. Initial reaction rates in *n*-octane, isooctane, isopropanol and water were represented by a Langmuir–Hinshelwood type kinetic equation, where the concentration of hydrogen in solution was calculated from a correlation developed for its solubility in mixtures of solvents. A very good agreement between the experimental and calculated rates of reaction is observed and the effect of the solvent is interpreted in terms of the rate constants.

INTRODUCTION

The use of Raney nickel as catalyst in organic reactions, mainly in hydrogenations, began in the 1930's. Early experiments showed that complete hydrogenation of acetone could be attained at room temperature and low pressure after only 11 hr and that the secondary alcohol was selectively obtained (*1*, *2*).

The first kinetic study on the hydrogenation of liquid acetone on Raney nickel in these conditions was made by Freund and Hulburt (*3*). It was shown that internal diffusion was controlling, the reaction order with respect to hydrogen was zero and the activation energy was 13 kcal/mol. Kishida and Teranishi (*4*) put forward a Langmuir–Hinshelwood type kinetics and assumed that the rate constant is the same in different solvents. Iwamoto *et al.* (*5*) made a similar study but also varied the hydrogen pressure. The true activation energy was found to be dependent on the solvent and varied between 7.4 and 10.3 kcal/mol. They tried unsuccessfully (*6*) to find a correlation between the reaction rate constant and a characteristic parameter of the solvent.

However, neither of the above studies has taken into account the change of hydrogen solubility with the composition of the solution. For a fixed hydrogen pressure, the solubility in acetone is half of that in saturated hydrocarbons and more than 10 times the value in water and, therefore, the values of the parameters obtained are not valid.

In the present work, the experimental rate of hydrogenation of acetone in several solvents is successfully interpreted by a Langmuir–Hinshelwood type equation, where the concentration of hydrogen is calculated from a correlation developed for the solubility of hydrogen in mixtures of solvents. The effect of solvent on the rate of reaction is interpreted in terms of the reaction rate constants.

NOMENCLATURE

a, b	parameters introduced in Eq. (11)
c	concentration, mol/cm^3
E_A	activation energy, kcal/mol
ΔE^v	molar energy of vaporization, cal/mol
f^L	fugacity of liquid, atm

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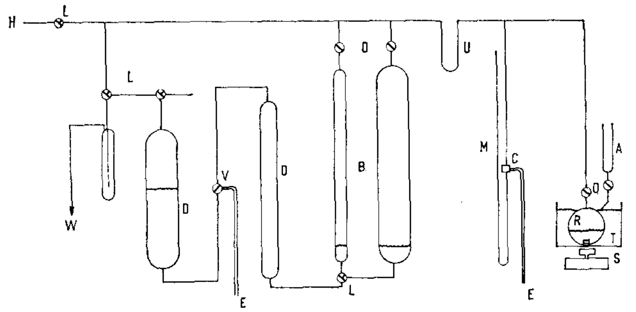

FIG. 1. Schematic diagram of the apparatus: (A) acetone reservoir; (B) gas burette; (C) electric cell; (D) dibutyl phthalate; (E) electric relay; (H) hydrogen cylinder; (L) three-way stopcock; (M) mercury manometer; (O) one-way stopcock; (R) reactor; (S) magnetic stirrer; (T) constant temperature bath; (U) U-tube with Na_2CO_3; (V) solenoid valve; (W) vacuum pump.

ΔH^a	molar enthalpy of adsorption, kcal/mol
ΔH^v	molar enthalpy of vaporization, cal/mol
K	adsorption constant, liters/mol
k	rate constant $(g\ s)^{1/2}/mol^{1/2}$
p	partial pressure of gas, atm
R	gas constant (=1.987 cal/mol K)
r	rate of reaction, mol/g s
S	sum of squares of errors $[=\Sigma(r_{exp} - r_{calc})^2]$, $(mol/g\ s)^2$
T	temperature, K
v	molar volume, cm^3/mol
x	mole fraction
β	parameter introduced in Eq. (4), mol/cm^3
δ	solubility parameter, $cal^{1/2}/cm^{3/2}$
δ^c	corrected solubility parameter, $cal^{1/2}/cm^{3/2}$
ϕ	volume fraction

Subscripts

A	acetone property
app	apparent value
calc	calculated value
H	hydrogen property
exp	experimental value
P	isopropanol property
S	solvent property

Superscript

0	pure liquid

EXPERIMENTAL PART

Description of the Apparatus

Hydrogenation rates were measured in a stirred glass reactor of 0.5 liter capacity. It was kept immersed in a constant temperature bath and its contents were stirred with a magnetic stirrer (Fig. 1). The reactor was connected to measuring gas burettes by means of a glass joint. The reaction rate was determined at constant pressure by measuring the dibutyl phthalate level in the gas burette. The pressure sensing device consisted of an electric cell attached to a mercury manometer. When a small change in the mercury height (less than 0.1 mm) was detected by the cell, a relay was activated and opened the valve, allowing the dibutyl phthalate to flow from its reservoir and adjust its level in the gas burette so that the pressure in the system remained constant. Once the pressure was restored to its original value, the relay closed the valve until a new cycle began. The level in the gas burette was automatically adjusted every 5–10 s and the pressure in the reactor could be fixed at any value up to atmospheric pressure and kept constant within an error of $\pm 10^{-4}$ atm. A more detailed description of the apparatus can be found elsewhere (*7*).

TABLE 1

Physical Properties of the Raney Nickel Catalyst[a]

Nickel content (%)	92
Surface area (m^2/g)	50
Porosity	0.51
Apparent density (g/cm^3)	4.5
Av particle diam (μm)	10

[a] The average particle diameter was measured experimentally. Remaining values of properties were supplied by the manufacturer.

Catalyst

The catalyst used was Raney nickel Nicat 102 supplied by Joseph Crosfield & Sons. It is obtained from a minus 200 mesh nickel–aluminum alloy. A summary of its physical properties is shown in Table 1. The average particle size, as supplied by the manufacturers, is 21 μm but for the kinetic measurements a sample of the smallest particles was separated by sedimentation. An analysis of the new particle size distribution was made with a Coulter counter Model A and the average size was found to be 10 μm. During the period the experiments were carried out, the catalyst was kept under water in a nitrogen atmosphere and at 5°C. Its activity was checked at the beginning and at the end of the kinetic measurements and no change was detected. All the experiments were carried out over a period of 3 months.

Procedure

A sample of the aqueous slurry of the catalyst containing 0.5–1.0 g of nickel was transferred to the reaction vessel, already weighed, and dried under vacuum for 1 hr at room temperature. The mass of Raney nickel was determined by weighing the vessel with the dry catalyst. The reactor was then introduced into a glove box with a nitrogen atmosphere where 20–50 ml of degassed solvent were added and finally it was connected to the measuring system. The whole apparatus was purged with hydrogen and filled to the required pressure. Once equilibrium was reached, degassed acetone was added to the reactor. Readings of the volume consumed were made every 15 s during the first 5 min and were plotted as a function of time. Initial rates of reaction were determined from the slopes of the straight lines obtained.

Experiments were carried out in two nonpolar solvents, namely, *n*-octane and 2,2,4-trimethyl pentane (isooctane), one polar, namely, isopropanol, and one which was highly polar, viz, water. Runs were made at 0, 7 and 14°C, except in the case of isooctane when experiments were carried out only at 7°C. The hydrogen pressure was varied from 10 to 60 cm Hg. The catalyst was renewed daily and measurements of the reaction rate in the same conditions at the beginning and at the end of the day were carried out. No definite trend was observed and the values obtained did not differ by more than 5%. The stirring of the reacting solution ensured that the temperature was uniform throughout the reactor. It was checked that the stirring did not affect the rate of reaction (*7*).

Preliminary experiments showed that no reaction occurred in the absence of catalyst and that, when Raney nickel was present, the only product of reaction was isopropanol.

Gradients of hydrogen and acetone concentration in the boundary layer surrounding the catalyst particle were determined to be lower than 1.4% and the effectiveness factor was estimated to be greater than

TABLE 2

Parameters in the Solubility Correlation

T (°C)	$\ln f_{H_2}{}^L$ (atm)	v_{H_2} (cm^3/mol)	δ_{H_2} ($cal^{1/2}/cm^{3/2}$)
0	6.246	22.9	2.1
7	6.174	24.1	2.1
14	6.106	25.2	2.1
25	5.982	26.8	2.1

TABLE 3

Comparison between Estimated and Experimental Hydrogen Solubilities in Various Solvents at 25°C and 1 atm

Solvent	ΔH^v (kcal/mol)	v (cm^3/mol)	δ (cal$^{1/2}$/cm$^{3/2}$)	δ^c (cal$^{1/2}$/cm$^{3/2}$)	$x_{H_2} \times 10^4$	
					(est.)	(exp.)
Acetone	7.604	73.3	9.8	9.2	2.545	2.390
n-Octane	9.914	162.5	7.6	—	6.373	6.832
Isopropanol	9.790	76.2	11.0	9.4	2.232	2.173
Isooctane	8.395	165.1	6.9	—	8.846	7.815
Water	10.481	18.0	23.4	12.7	0.152	0.142

0.99 (*7*). It can also be shown that the catalyst operated isothermally (*7*).

ANALYSIS OF RESULTS

Correlation for Hydrogen Solubility in Liquid Mixtures

The difficulty in developing a theory to understand the solutions of nonreacting gases in liquids and liquid mixtures has been partially overcome by several attempts to correlate the values of solubility of the gas with the properties of the solvents. A general review on this subject has been given by Battino and Clever (*8*).

Prausnitz and Shair obtained a good correlation for the solubility of gases in nonpolar systems (*9*). They put forward for pure gas A dissolving at atmospheric pressure and temperature T in solvent 1 the equation,

$$-\ln x_A = \ln f_A{}^L\,(1\text{ atm}) + \frac{v_A(\delta_1 - \delta_A)^2}{RT}, \quad (1)$$

where $f_A{}^L$ is the fugacity (atm) of pure "liquid A," v_A the molar volume of pure "liquid A," and δ_1 and δ_A the solubility parameters of the solvent and the condensed gas, respectively. The solubility parameters are proportional to the cohesive energy densities of the liquids and are calculated from

$$\delta = \left(\frac{\Delta E^v}{v}\right)^{\frac{1}{2}} = \left(\frac{\Delta H^v - RT}{v}\right)^{\frac{1}{2}}, \quad (2)$$

where ΔE^v is the molar energy and ΔH^v the molar enthalpy of vaporization.

In the above equation three of the parameters, namely, $f_A{}^L$, v_A and δ_A, must be obtained from solubility data. Since several sets of them will satisfactorily represent experimental results, it is sensible to accept a priori the value of 2.1 for the solubility parameter of liquid hydrogen (*10*b). By applying a least squares method to available data for fluoroheptane, isooctane, n-octane, n-heptane, toluene and benzene (*8*), values of the remaining parameters, namely $f_A{}^L$ and v_A, are obtained at different temperatures and are summarized in Table 2.

However, Eq. (1) only holds for solutions of hydrogen in nonpolar solvents and, since we are also interested in estimating the solubility in polar solvents and their mixtures, the solubility parameter will be modified in order to extend the correlation. From solubility data in acetone, isopropanol, methanol and water, a correction factor arises so that the solubility parameter for polar liquids with $\delta > 9.0$ is given by

$$\delta^c = \frac{\delta}{1.772\log(\delta - 2.1) - 0.509}. \quad (3)$$

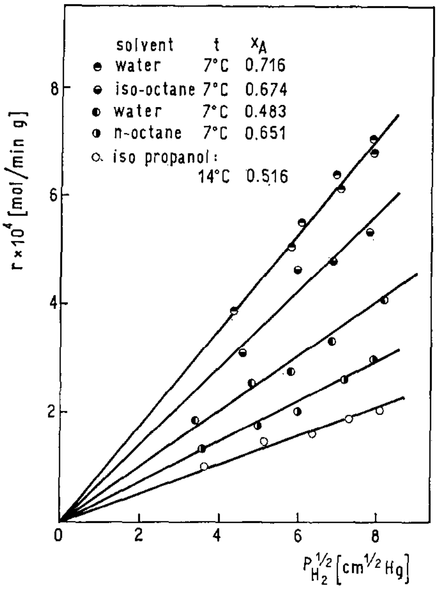

FIG. 2. Order of reaction with respect to hydrogen.

If we compare the estimated solubility arising from Eqs. (1) and (3) with experimental values (*8*) we find they agree reasonably well (Table 3).

Up to now we have only dealt with solutions of gases in pure liquids. For solvent mixtures (liquids 1 and 2), Hildebrand *et al.* (*10*a) suggest that a good estimation of the solubility of the gas is obtained by applying the expression,

$$\ln x_{A,\mathrm{mix}} = \phi_1 \ln x_{A,1} + \phi_2 \ln x_{A,2} - v_A \beta_{12} \phi_1 \phi_2, \quad (4)$$

where $\beta_{12} = (\delta_1 - \delta_2)^2/RT$ and ϕ_i represents the volume fraction of component i, $\phi_i = x_i v_i / \Sigma x_i v_i$. In case one or more solvents are polar, the solubility parameter will be calculated from Eq. (3).

When the gas pressure is no longer 1 atm, it can be shown (*7*) that

$$x_A = x_A(1\ \mathrm{atm}) p_A, \quad (5)$$

where p_A is the partial pressure of gas A.

Kinetic Equation

Anderson and MacNaughton (*1*) studied the hydrogenation of acetone on various catalysts using a mixture of hydrogen and deuterium as reducing agent. They were able to determine that at low temperatures and on Raney nickel hydrogen adds to the keto form. Previous kinetic measurements suggest that the reaction mechanism can be described (*4*, *5*) according to the following steps

$$\begin{aligned} A + 1 &= A1, \\ H_2 + 21 &= 2H1, \\ A1 + H1 &= AH1 + 1, \\ AH1 + H1 &= P1, \\ P1 &= P + 1, \end{aligned} \quad (6)$$

where A, AH and P describe the acetone, monohydrogenated acetone and isopropanol, respectively, and 1 denotes an active site.

Assuming Langmuir isotherms of adsorption for all the components and that the first step in the surface reaction is controlling, we obtain

$$r = \frac{k_1 K_A K_H^{\frac{1}{2}} c_A c_{H_2}^{\frac{1}{2}}}{(1 + K_A c_A + K_H^{\frac{1}{2}} c_{H_2}^{\frac{1}{2}} + K_P c_P + K_S c_S)^2}, \quad (7)$$

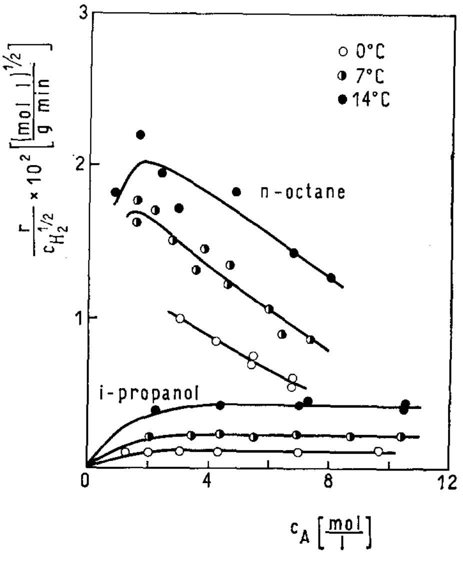

FIG. 3. Rates of hydrogenation in *n*-octane and isopropanol.

where $K_S c_S$ represents the adsorption of the solvent on the catalyst. The surface concentration of AH was neglected in the derivation of Eq. (7) because initial rates of reaction were measured in all experiments. When isopropanol is used as solvent, the surface concentration of monohydrogenated acetone can be neglected with respect to the sum of surface concentrations of the stable species, acetone and isopropanol.

Simonikova *et al.* (*11*) studied the same reaction in the gas phase over different metal catalysts and found that the adsorption constant of hydrogen is between 10 and 100 times lower than for acetone. In addition, since the concentration of hydrogen in the liquid phase is 10^{-3} times lower than for acetone, the expression for the rate of reaction can be reduced to

$$r = \frac{k_1 K_A K_H^{\frac{1}{2}} c_A c_{H_2}^{\frac{1}{2}}}{(1 + K_A c_A + K_P c_P + K_S c_S)^2}. \quad (8)$$

From this equation an order of one half with respect to hydrogen arises. Therefore, the rate of reaction was plotted as a function of the square root of the hydrogen concentration (or pressure) for a fixed acetone concentration. For all solvents straight lines were obtained, confirming that the first step in the surface reaction is rate-controlling (*7*) (Fig. 2).

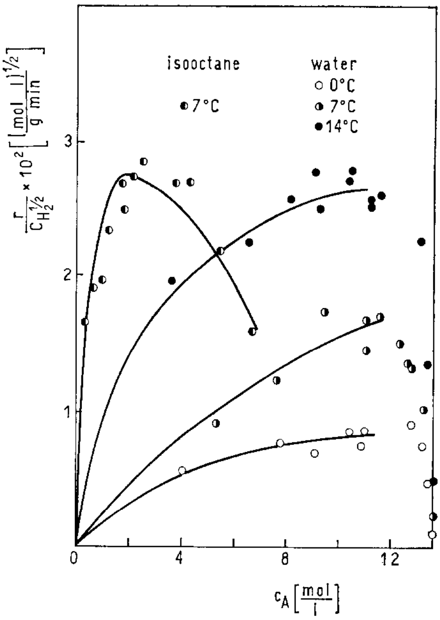

FIG. 4. Rates of hydrogenation in water and isooctane.

Parameter Estimation

In order to estimate the values of the parameters in Eq. (8) which best represent the experimental results (Figs. 3 and 4), a nonlinear regression was applied. Since the concentrations of acetone and solvent in the starting mixture are related by $x_A = 1 - x_S$ and accepting that the total molar concentration is proportional to the concentration of acetone, it follows that

$$c_S = c_S^0 - \frac{c_S^0}{c_A^0} c_A , \quad (9)$$

where c_S^0 and c_A^0 are the molar concentrations for pure solvent and pure acetone, respectively. Initial rates will be given by

$$r = \frac{k_1 K_A K_H^{\frac{1}{2}} c_A c_{H_2}^{\frac{1}{2}}}{(1 + K_S c_S^0 + (K_A - K_S c_S^0/c_A^0) c_A)^2}, \quad (10)$$

and redefining the parameters

$$r = \frac{c_A c_{H_2}^{\frac{1}{2}}}{(a + b c_A)^2} \quad (11)$$

where $a = (1 + K_S c_S^0)/(k_1 K_A K_H^{\frac{1}{2}})^{\frac{1}{2}}$ and $b = (K_A - K_S c_S^0/c_A^0)/(k_1 K_A K_H^{\frac{1}{2}})^{\frac{1}{2}}$.

From the expression above only two parameters can be estimated, while in the original equation we have three, namely $k_1 K_H^{\frac{1}{2}}$, K_A and K_S. A procedure to overcome this problem is explained in the following section.

Isopropanol, n-Octane and Isooctane as Solvents

From several studies of metal catalyzed reactions involving aliphatic hydrocarbons

TABLE 4

Parameters Estimated by Nonlinear Regression

Solvent	T (°C)	a	b (liters/mol)	S (mol/min g)^2	$k_1K_H^{1/2}$ [(liter mol)$^{1/2}$/min g]	K_A (liters/mol)
n-Octane	0	5.05	4.19	7.76×10^{-9}	0.0472	0.830
	7	4.37	3.31	3.92×10^{-8}	0.0692	0.757
	14	4.88	2.50	2.14×10^{-8}	0.0816	0.515
						K_S
Isooctane	7	4.04	2.25	1.87×10^{-7}	0.140	0.0523
Isopropanol	0	31.10	6.50	2.70×10^{-10}	0.0128	0.168
	7	23.67	4.65	2.05×10^{-10}	0.0225	0.159
	14	17.70	3.14	5.81×10^{-10}	0.0342	0.103
Water	0	21.18	1.41	3.72×10^{-9}	0.111	0.098
	7	21.63	0.383	1.90×10^{-8}	0.234	0.146
	14	10.44	0.909	2.48×10^{-8}	0.239	0.048

and of their adsorption on Raney nickel (*4, 12, 13*) it has been concluded that their adsorption constants are negligible compared with that of acetone. When the regression is carried out with the results obtained in n-octane, K_S will be taken as zero and therefore

$$k_1K_H^{1/2} = 1/ab \quad K_A = b/a. \tag{12}$$

Once the value of K_A has been obtained, both the rate constants in isopropanol and isooctane and their adsorption constants are obtained from

$$K_S = \frac{K_A - b/a}{(b/a)c_S^0 + c_S^0/c_A^0}$$
$$k_1K_H^{1/2} = \frac{1}{K_A}\left(\frac{1 + K_Sc_S^0}{a}\right)^2. \tag{13}$$

A linear regression of the experimental results was carried out first, with the rate of reaction equation in the form

$$\left(\frac{c_Ac_{H_2}^{1/2}}{r}\right)^{1/2} = a + bc_A, \tag{14}$$

and the concentration of hydrogen in solution was calculated from the solubility correlation [Eqs. (1), (3), (4) and (5)]. The estimated values of a and b are used as initial guesses for the nonlinear regression.

The nonlinear regression was carried out for each solvent at the different temperatures and the sum of squares of errors was minimized. A computer program "Least squares estimation of nonlinear parameters" based on an algorithm developed by Marquardt (*14*) was used, and the results obtained are summarized in Table 4.

The solvent effect on the rate of reaction is essentially reflected in a change in the activities of the reacting species in solution, and therefore the rate constant will vary with a change of solvent (*15*). It can be seen in Table 4 that the highest value corresponds to water, but this can be attributed, as explained below, to a change in the structures of the adsorbed substances. For the remaining solvents a decreasing rate of reaction constant is observed for the series isooctane > n-octane > isopropanol, which corresponds to increasing values of the solubility parameter δ and the dielectric constant ϵ, as is generally observed in homogeneous reactions (*15*). However, those equations generally used in this case did not represent adequately the solvent effect. This can be attributed to the influence of the electronic field of the catalyst.

Water as Solvent

When water is added to acetone a very large increase in the rate of hydrogenation is observed. Further increases in the concentration of water decreases the measured rate (Fig. 4). Analysis of the solubility of hydrogen in acetone–water mixtures shows that it decreases from pure acetone to pure water, without explaining the effect observed in the consumption of hydrogen.

Selyakh and Dolgov (*16*) suggested that the water promotes the enolization of the adsorbed acetone and, since the double bond C=C is more readily hydrogenated than the carbonyl group, an increase in the rate of reaction must be observed. No enolization of acetone is detected in aqueous solution in the absence of a catalyst (*15*) but since in the adsorbed state a rearrangement of electrons is occurring, the existence of the enol form as reactant for the hydrogenation is possible.

At the same time, it is widely accepted that hydrogen is adsorbed on the solid with two different strengths, the strongly bound one being mainly responsible for the carbonyl reduction (*17*, *18*). In a study of the hydrogenation of benzalacetone on Raney nickel, Sokol'skii and Erzhanov (*18*) found that the addition of water increases the carbonyl reduction rate and an increase in the amount of hydrogen adsorbed is suggested to be the cause. The observed effect can also be attributed to a change in the ratio of the two different forms of adsorbed hydrogen, so that the strongly bound one required for the carbonyl hydrogenation is favored.

It follows that the addition of water changes the structure of the adsorbed substances, but a more detailed study on this subject is necessary. However, since it is reasonable to assume that changes in the adsorption and reaction rate constants occur only at high acetone concentrations, in order to determine the parameters in the kinetic equation we will consider the data for concentrations of acetone below 11 mol/liter. A nonlinear regression was applied, as explained above, and the estimated parameters are indicated in Table 4.

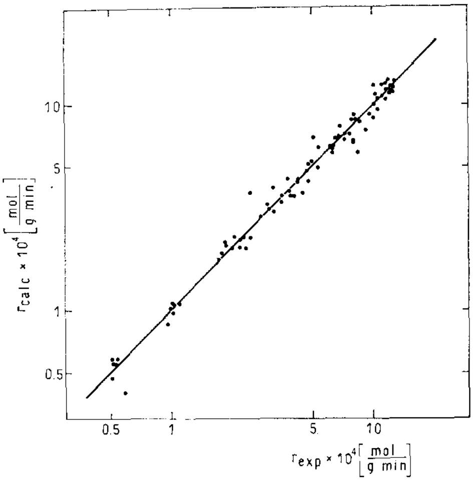

FIG. 5. Calculated vs experimental rates of reaction.

Comparison of Results

In order to analyze the fitting of the results by the proposed kinetic equation, the calculated rates of reaction for all solvents are plotted as a function of the experimental ones in Fig. 5. A very good agreement is observed.

In addition, the validity of the adsorption constants arising from the kinetic equation can be checked by comparing with values from adsorption measurements. If we compare the ratio of constants at 14°C (Table 4) with the one determined by Delmon and Balaceanu (*19*), we find a reasonable agreement. For the system acetone–water the ratios are 10.7 and 21, while for acetone–isopropanol, 5.1 and 3, respectively.

Heats of Adsorption and Activation Energies

The heats of adsorption can be determined from the estimated adsorption constants. The values for isopropanol, acetone and water are 5.5, 5.3 and 8.0 kcal/mol, respectively (*7*), and they are higher than those expected if the adsorbed species were held by ordinary dispersion forces, suggesting also that chemisorption of acetone does not take place and that the C=O bond is not broken during the adsorption.

The apparent activation energies can be related to the true ones according to

$$E_{A_{app}} = -\frac{d \ln k_{app}}{d(1/RT)} = -\frac{d \ln k_1}{d(1/RT)} - \frac{1}{2}\frac{d \ln K_H}{d(1/RT)} = E_A - \tfrac{1}{2}\Delta H_H{}^a, \quad (15)$$

where $\Delta H_H{}^a$ represents the heat of adsorption of hydrogen. The apparent activation energies determined in *n*-octane, isopropanol and water are 6.2, 11.0 and 8.6 kcal/mol, respectively (*7*). Similar values have been determined in previous research work (*3*).

The heat of adsorption of hydrogen from the gas phase on nickel was found to range from 15 to 30 kcal/mol (*12*, *17*). No data on the heat of adsorption of hydrogen from solution is available, but since dissociation of the molecule takes place during the adsorption, it is expected not to be very much smaller than the values given above. This justifies the rather low values obtained for the activation energy, in particular in *n*-octane. The true ones will be about *5–8* kcal/mol higher.

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