JOURNAL OF CATALYSIS **133**, 21–27 (1992)

Linear Free Energy Relationships in the Reduction of Imines over a Pd/Sepiolite Catalyst

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Received March 1, 1991; revised July 11, 1991

In this work we synthesized a series of imines of formula R–C_6H_4–CH=N–C_6H_5 and C_6H_5–CH=N–C_6H_4–R (R = OH–, CH_3O–, CH_3–, HOOC–, CH_3–CO, and CH_3–COO–) and subjected them to hydrogenation with H_2 over a 3% Pd catalyst supported on sepiolite extracted from Vallecas (Madrid, Spain). From the relationships found between ln A and E_a we inferred the occurrence of a compensating effect in the process. We also determined the influence of substituents on the reduction rate from the σ contributions reported by Hammett.

By taking N-benzylideneaniline as a reference, we found the presence of electron-withdrawing substituents in either aromatic ring increased the rate of reduction of the >C=N–bond, while that of electron-releasing groups had the opposite effect. Substituents on the benzylidene ring were found to have a more marked effect than those on the phenylimine ring.

A general multi-step reduction pathway similar to that reported by Horiuti–Polanyi (*Trans. Faraday Soc.* **30,** 1164 (1934)) is proposed to account for the experimental results obtained.

INTRODUCTION

Kinetic or mechanistic studies on heterogenous catalysis frequently involve the use of models which allow linear free energy relationships (LFER) of Brønsted, Taft, or Hammett type (*1*) to be obtained.

The so-called "compensating effect" is one other of such models and can be derived from the Arrhenius equation in the form

$$\log A = B + eE_a,$$

where B and e are two characteristic constants of the group of reactions and/or catalysts concerned. In the event that changes in one of these parameters result in concomitant changes in the other, the process is said to be subject to a "compensating effect." This phenomenon was first reported by Constable in 1925 (*2*) for the hydrogenation of ethanol over copper catalysts and since then has been studied by a number of authors (*3–7*).

The compensating effect can be studied from the point of view of the substrates or of the catalysts used (*8*). Reactions subject to compensating effects share some common features in relation to the reactants or products, or the catalytic phase. However, authors have so far resorted to more discrepant explanations to account for it. Thus, some ascribe it to the occurrence of a characteristic temperature at which the adsorption, dissociation, or surface mobility of the reactants or reaction intermediates is significant enough to influence the catalytic effect (*9, 10*). Others (*11, 12*) attribute this effect to the involvement in the process of active sites of different energy which result in average A and E_a values. Still other authors assign the relationship between A and E_a to a variation in the concentration of active sites with the temperature (*13*) or to changes in the coefficients of activity of the adsorbed species (*14*), or even to variations in the

0021-9517/92 $3.00

energy contents of the reactants through formation of surface dipoles (*15*). According to Galwey (*6*), the above explanations are not mutually exclusive.

Linear free energy relationships for a given process can also be derived from the Hammett equation (*16*) expressed in the form

$$\log K/K_0 = \rho\sigma,$$

where K is the rate constant of the process in question, K_0 the K value for the reference compound, ρ the specific rate of reaction, and σ the electric contribution from the substituent (*17*). This equation has been applied to a host of processes taking place in homogeneous and heterogeneous phases such as the hydrogenation of substituted nitrobenzenes over Pd (*18*) or Pt catalysts (*19*) and that of alkylbenzenes over Pt catalysts (*20*), various condensations of aromatic aldehydes and ketones over $AlPO_4$ solids (*21*), etc.

The more free energy correlations for a process that can be found, the easier it is to understand its mechanism.

The hydrogenation of imino groups has been studied by several authors (*22*) using metal hydrides (*23*) or dihydrogen (*24*), or by hydrogen transfer with inorganic donors (*25*) or complex donors approaching biomimetic synthesis (*26*). Roe and Montgomery (*27*) applied the Hammett equation to the hydrogenation of various aromatic imines over platinum catalysts, but they obtained ρ values varying over rather a wide range. On the other hand, Steeven and Pandit (*28*), who investigated the reduction of various imines by transfer using Hanstzsch's ester as donor, obtained results conformant to the Hammett equation.

In this work we carried out the hydrogenation of various imines of formula $R{-}C_6H_4{-}CH{=}N{-}C_6H_4{-}R'$ over a Pd catalyst supported on sepiolite and established different free energy correlations on the basis of which a reduction mechanism for the process is proposed.

EXPERIMENTAL

Catalyst

The catalyst used consisted of 3% w/w Pd supported on sepiolite from Vallecas (Madrid, Spain) and supplied by TOLSA S.A. (S_{BET} = 280 m^2/g; average pore radius = 35 Å). The acidity and basicity were determined by a spectrophotometric method involving the quantitation of titrating agent adsorbed in a monolayer form by constructing a liquid-phase Langmuir isotherm (*29*). The acidity against pyridine was found to be 7.1×10^{-5} mol g^{-1}, while the basicity against *m*-nitrobenzoic acid was 27.9×10^{-5} mol g^{-1}. The catalyst was synthesized by impregnation from an aqueous solution of $(NH_3)_4PdCl_2$. Once the salt was deposited on the support, it was dried in a stove at 110°C for 24 h, after which it was reduced by raising the temperature linearly—under a hydrogen stream flowing at a rate of 50 ml/min—at 1 K/min up to 573 K, which was maintained for a further 90 min. The metal surface area of the catalyst thus obtained was determined by X-ray diffraction on a Phillips 1130/00/60 instrument by using CuK_α radiation at λ = 1.5418 Å. The half-peak width was calculated graphically at an angle 2θ = 40.1° corresponding to the (111) plane of Pd, and assuming constant K in the Debye–Scherrer equation (*30*) to be equal to 0.89.

The metal surface area of the catalyst thus obtained by applying the cubic particle model was 59 m^2/g_{Pd}.

Synthesis of the Reactants

The imines used were not commercially available products, so they had to be synthesized prior to the experiments (*3*). Thus, we prepared various imines with different substituents on the imino bond, viz. p-$X{-}C_6H_4{-}CH{=}N{-}C_6H_5$ and $C_6H_5{-}CH{=}N{-}C_6H_4{-}X$-$p$, where X denotes the different substituents ($-OH$, $-OCH_3$, etc.). Other imines included one or two non-aromatic substituents bound to the imino function.

TABLE 1

Initial Rate of Hydrogenation ($10^5\ r$, mol/s m^2_{Pd}) of Imines of Formula p-R–C_6H_4–CH=N–C_6H_4–R′-p

R	R′	σ	r_{303}	r_{313}	r_{323}	r_{333}
-H	-H	0	3.8	5.3	6.9	9.5
$-CH_3$	-H	−0.17	2.6	3.8	5.1	7.0
$-OCH_3$	-H	−0.27	1.5	2.5	3.2	4.6
-OH	-H	−0.37	1.2	1.8	2.6	3.7
-COOH	-H	0.45	4.0	5.5	7.1	9.7
-H	$-CH_3$	−0.17	3.3	4.5	6.1	8.5
-H	$-OCH_3$	−0.27	3.1	4.1	5.9	8.0
-H	-OH	−0.37	2.9	3.8	5.6	7.8
-H	$-COOCH_3$	0.45	4.4	5.8	7.4	9.8
-H	$-COCH_3$	0.50	4.7	5.9	7.8	10.2

Note. Conc: 0.5 *M*; V_T = 20 ml; P(H_2) = 5 bar; amount of catalyst = 0.05 g. Subscripts to *r* denote reaction temperatures (in K).

Catalytic Activity

Hydrogenation runs were carried out in an ordinary low-pressure Gerhardt hydrogenator furnished with a pressure gauge for continuous monitoring of the hydrogen pressure within the reaction vessel. Reactions were accomplished by using 20 ml of 0.5 *M* solutions in methanol at 323 K and an initial hydrogen pressure of 5 bar. An amount of catalyst of 0.05 g, reactant concentrations over the range 0.3–0.6 *M*, pressures between 3 and 6 bar, and temperatures from 303 to 333 K were used in studying the effect of the kinetics of the process. The reaction temperature was controlled by pumping water from a thermostatic bath through the vessel jacket.

The reaction rate was determined from the initial slope of the variation of the hydrogen pressure as a function of time. Blank runs were performed prior to obtaining any kinetic data in order to check for the absence of phenomena other than those typical of the catalytic process. Neither the support nor any other part of the reactor used proved to be active in the reduction of benzylideneaniline. Also, no diffusion phenomenon was observed on shaking at a rate of over 200 shakes/min, and no interparticle diffusion was found to occur while working with catalyst sifted through 70–230 mesh.

The rate of hydrogen transfer from the gas phase to the reaction medium was checked not to be the rate-determining step of the process. Under the working conditions used, the initial rate of reaction was found to increase linearly with the amount of catalyst used.

Product Analysis

The reaction products obtained were analysed on a Hewlett-Packard 5830A chromatograph fitted with an HP 18850 GC terminal. The chromatographic column was packed with 5% Carbowax 20 M on 80/100 Chromosorb G-AWDMCS. The nature of the products was confirmed by coupling the GC instrument to a Hewlett-Packard 5992B mass spectrometer.

The secondary amine corresponding to the hydrogenation of the imino double bond (>C=N–) was the sole reaction product obtained in every instance. None of the substituents on the aromatic rings was found to be altered, nor were any products from potential hydrogenolysis reactions detected.

RESULTS AND DISCUSSION

Tables 1 and 2 list the initial hydrogenation rates of the different imines studied at the four reaction temperatures assayed for

TABLE 2

Initial Rate of Hydrogenation ($10^5\, r$, mol/s m^2_{Pd}) of Imines with Aliphatic Groups

Substrate ($Z + E$)	r_{303}	r_{313}	r_{333}	r_{343}
C_6H_5–CH=N–Cy	0.9	1.4	2.1	3.0
Cy–CH=N–C_6H_5	0.6	0.9	1.4	2.1
Cy–CH=N–Cy	0.1	0.2	0.3	0.5
C_6H_5–CH=N–But	1.6	2.3	3.3	4.7

Note. For conditions, see Table 1; Cy = cyclohexyl, But = butyl.

the imines bearing two aromatic and one or two aliphatic substituents on the imino bond, respectively.

As can be seen, if N-benzylideneaniline is taken as reference, the presence of electron-withdrawing substituents on either ring results in increased reaction rates, while that of electron-releasing groups has the opposite effect. Also, electron-releasing groups on the benzylidene ring have more marked effects than those on the phenylimino ring. Hence, reaction development appears to be increased by the presence of groups decreasing the electron density on the imino bond; conversely, groups increasing the electron density cause the reaction rate to decrease, irrespective of the position of the aromatic ring in the imino bond. In order to check this assumption we carried out reactions involving the imines listed in Table 2. Alternative substitution of each aromatic ring in benzylideneaniline by a cyclohexyl ring invariably resulted in a decrease in the reaction rate with respect to that obtained for the parent compound. On the other hand, the effect was more marked when the substituted aromatic ring was bound to the carbon atom rather than the nitrogen atom.

Table 3 lists the activation energies and pre-exponential factors obtained for the hydrogenation of the different imines studied as calculated from the Arrhenius equation. The order of activation energies is virtually opposite that of the rates, i.e., the activation energies of benzylideneanilines with electron-withdrawing substituents are higher than those bearing electron-releasing substituents. Also, the imines including aliphatic groups have higher activation energies that those bearing aromatic substituents alone.

The data in Table 3 prompt the occurrence of a compensating effect. Figure 1 shows a plot of ln A vs E_a. As can be seen, the results fit a straight line, which allows one to assume that these reactions are subject to a compensating effect, so their mechanisms must be quite similar.

From the general expression of the compensating effect (*6*)

$$\ln A = \ln \alpha + E_a/R\theta$$

we calculated θ and α, the latter of which is the rate of reduction of each substrate at the isokinetic temperature (θ). Insofar as this last did not lie within the temperature range studied and the E_a range was quite wide, we may state that the assumed compensating effect did actually occur.

In order to quantify the effect of the substituents on the reaction rate of a series of related compounds it is customary to use the Hammett equation. However, the formulation of this equation has some con-

TABLE 3

Values of ln A and E_a Obtained in the Hydrogenation of the Different Imines Studied

Substrate ($Z + E$)	ln A	E_a (kJ/mol)
ϕ–CH=N–ϕ	−0.2	25
p-CH_3–ϕ–CH=N–ϕ	0.5	28
p-CH_3O–ϕ–CH=N–ϕ	0.9	30
p-HO–ϕ–CH=N–ϕ	1.2	32
p-HOOC–ϕ–CH=N–ϕ	−0.6	24
ϕ–CH=N–ϕ–CH_3-p	0.2	26
ϕ–CH=N–ϕ–OCH_3-p	0.2	27
ϕ–CH=N–ϕ–OH-p	0.5	28
ϕ–CH=N–ϕ–$COOCH_3$-p	−1.3	22
ϕ–CH=N–ϕ–$COCH_3$-p	−1.3	22
ϕ–CH=N–But	1.2	31
ϕ–CH=N–Cy	1.5	33
Cy–CH=N–ϕ	2.8	38
Cy–CH=N–Cy	5.6	49

Note. ϕ = phenyl, Cy = cyclohexyl, But = butyl.

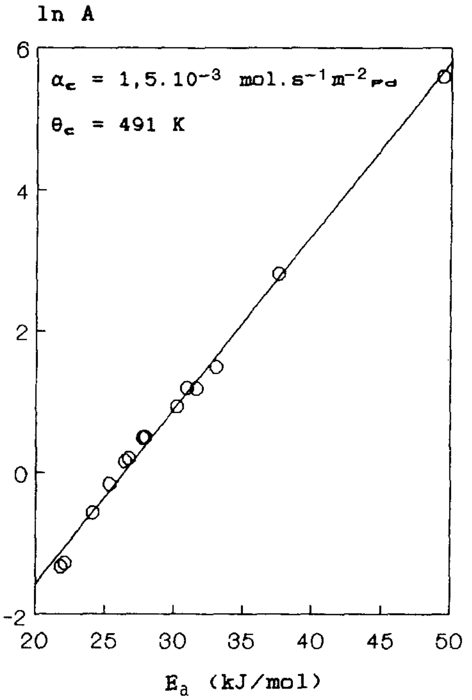

FIG. 1. Compensating effect on the hydrogenation of various imines.

straints imposed by narrow temperature ranges. Some authors (*32, 33*) have pointed out the need for alternative formulations in order to derive chemically significant LFERs for a series of reactions. Thus, according to Bernal *et al.* (*34*), a true LFER implies the existence of linear correlations between $\ln A$ and σ, and between E_a and σ, and hence the occurrence of a compensating effect. In order to derive such correlations, the above authors propose the following equations,

$$\ln A = \ln A_0 + \rho_\infty \sigma \qquad (1)$$

$$E_a = (E_a)_0 + \rho_\infty \theta R \sigma, \qquad (2)$$

where ρ_∞ is the specific rate of reaction at infinite temperature and R is a measure of the influence that the substituents would have at high temperatures.

Figures 2 and 3 show the fittings of our experimental results to Eqs. (1) and (2). As can be seen, there is good linearity for the imines with substituents on the ring bound either to the nitrogen atom or to the carbon atom of the imino bond. Only the imine bearing a carboxyl substituent on the benzylidene ring deviates somewhat from this behaviour, which can be ascribed to the possibility of the free carboxyl group being adsorbed at basic sites of the catalyst—this is probably not the case with the other substituents.

From these plots we obtained ρ_∞. The sensitivity of the imino bond to reduction is higher in those imines with substituents on the benzylidene ring ($\rho_\infty = -3.83$) than in those with substituents on the phenylimino ring ($\rho_\infty = -2.13$).

In previous work we found the kinetics of these reactions to be of zero-order in the substrate and of between zero- and first-order in the hydrogen pressure over the temperature range studied (*35*). This suggests the possibility that the catalyst surface may be saturated with imine and hydrogen may

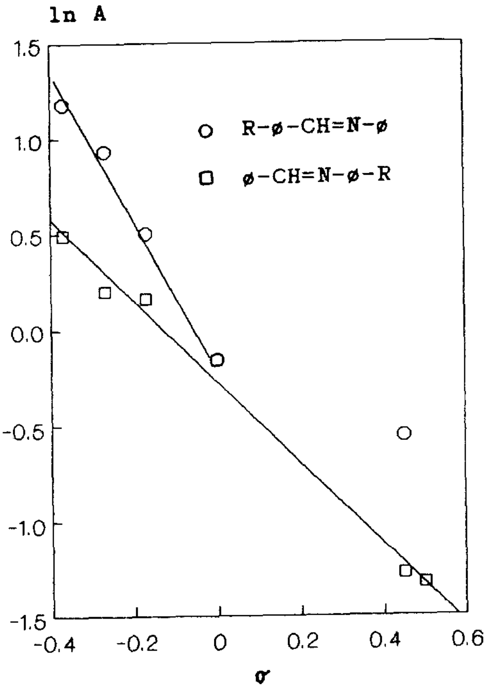

FIG. 2. Correlation between $\ln A$ and σ in the reduction of substituted aromatic imines.

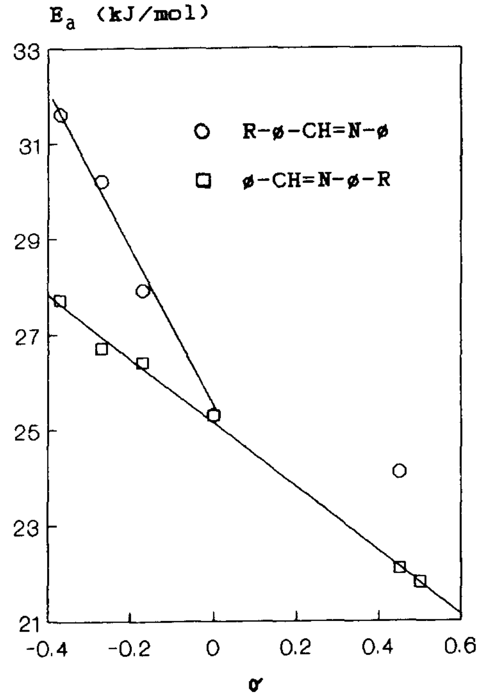

FIG. 3. Correlation between E_a and σ in the reduction of substituted aromatic imines.

be adsorbed non-competitively at the free sites not occupied by the substrate. Thus, we propose the following general reaction scheme for the reduction of imines, similar to that reported by Horiuti–Polanyi (*36*):

$$>C{=}N- + 2^* \rightarrow\ >C{=}N-_{ads} \qquad \text{(I)}$$

$$H_2 + 2^* \rightarrow 2H_{ads} \qquad \text{(II)}$$

$$>C{=}N-_{ads} + H_{ads} \rightarrow\ >\dot{C}-N <^{H}_{ads} + {*}\,(a) \qquad \text{(IIIa)}$$

$$>C{=}N-_{ads} + H_{ads} \rightarrow\ >CH-\dot{N}-_{ads} + {*}\,(b) \qquad \text{(IIIb)}$$

$$(a) \text{ or } (b) + H_{ads} \rightarrow\ >CH-NH- + 2\,{*}. \qquad \text{(IV)}$$

The occurrence of a compensating effect and the electronic contributions of the substituents of the aromatic benzylideneaniline support the above scheme for the reduction of all the imines studied. The process appears to take place mainly via steps (I), (II), (IIIa), and (IV).

The semi-hydrogenated species produced in (IIIa) would be more sensitive to the stabilizing or destabilizing effect of the substituents than that resulting from (IIIb), as one can infer from the results obtained. The addition of a hydrogen atom to the adsorbed imine in Step (IIIa) would yield a radical species on the surface that would be stabilized by the presence of electron-withdrawing groups on the aromatic ring bound to the carbon atom of the imino bond.

ACKNOWLEDGMENT

The authors gratefully acknowledge financial support from DGICyT (Project PB89-0340) for the realization of this work.

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