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# Reduction of Acetophenones over Pd/AlPO$_4$ Catalysts. Linear Free Energy Relationship (LFER)

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We studied the reduction of variously substituted acetophenones over Pd/AlPO$_4$, Pd/AlPO$_4$–SiO$_2$, and Pd/SiO$_2$ catalysts containing 3% Pd by weight. After the catalysts were characterized texturally and kinetically, they were used to reduce the different acetophenones at various temperatures under the same reaction conditions. The results correlate with the Hammett equation quite well, and the reaction was found to feature different sensitivity to electron-withdrawing ($0.05 < \rho < 0.20$) and electron-releasing substituents ($0.76 < \rho < 1.37$). On the other hand, a compensating effect was also found to occur, so the reaction mechanism can be assumed to be the same for every substrate. The reductions probably do not take place via enol forms of the acetophenone. The reaction rate decreases with increasing solvent polarity. © 1993 Academic Press, Inc.

## INTRODUCTION

Reductions of carbonyl compounds are of great interest to and widely used in organic chemistry. Such is the case with Wolff–Kishner and Clemensen reductions, whereby a carbonyl group is transformed into a methylene function by using hydrazine in a basic medium or zinc amalgam in hydrochloric acid, respectively, and the use of metal hydrides to convert aldehyde and ketones into their corresponding alcohols (*1*), and of alkali metals in ammonia to transform the carbonyl group into a methylene radical (*2*). Depending on the type of reductant used, the carbonyl function can be converted into a hydroxyl or methylene group as required. The hydrogenation of $\alpha,\beta$-unsaturated carbonyl compounds can be effected quite selectively on the carbon–carbon double bond or the carbon–oxygen bond (*3*, *4*). Carbonyl compounds can also be reduced with dihydrogen under homogeneous (*5*) or heterogeneous catalysis (*6*), as well as by hydrogen transfer. The most interesting asset of this process is the possibility of changing the selectivity toward the alcohol or the saturated hydrocarbon by changing the catalyst structure or the way in which the hydrogenation is performed (*8*, *9*).

Generally speaking, the reaction mechanisms proposed so far to account for the reduction of carbonyl compounds with hydrogen–metal systems are of the Horiuti–Polanyi type (*10*). The hydrogen atoms adsorbed on the metal, after dissociation, reduce the adsorbed carbonyl compounds stepwise. However, there is no universal agreement as to the nature of the active sites involved. While the sites where the aldehyde or ketone is converted into the alcohol, and this last in turn is transformed into the saturated compound, might be the same, the occurrence of sites of different nature on the edges and at the apices of the crystals (*11*, *12*) could be indicative of a different catalytic behaviour of the sites in question in hydrogenation and hydrogenolysis reactions.

The reduction mechanism supposedly involves the attack of the carbonyl compound by hydride ions and protons successively generated on the catalyst surface by adsorption of hydrogen atoms at high and low

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electron density sites, respectively (*13, 14*). This mechanism is inspired by that widely accepted for the reduction of metal hydrides, the first step of which involves the attack of a hydride ion on the carbonyl compound.

Alternatively, the reduction could take place via the enol form of the carbonyl compound in equilibrium with the oxo form. In this respect, Teratani *et al.* (*15, 16*) studied the deuteration of 1-cyclohexenyl methyl ether and cycloalkanones over different catalysts and arrived at different conclusions depending on the catalyst used. With Ru, Os, Ir, and Pt catalysts, the addition of two deuterium atoms to the carbonyl group was the prevailing processes, whereas with Pd and Rh catalysts, the deuterium atoms incorporated themselves at positions $C_2$ and $C_6$. On the other hand, Acke and Anteunis (*17*) detected enol intermediates and charged semihydrogenated species on the basis of which they accounted for the formation of alkanes, alcohols, and ethers.

One way of approaching the reaction mechanism proposed for the reduction of a series of homologous compounds is to determine whether the reaction features a linear free energy relationship—the equations most widely used in this respect on account of their simplicity are those of Brönsted, Taft and Hammett (*18*)—and is subjected to a compensating effect.

Linear free energy relationships for a given process can also be derived from the Hammet equation in the form

$$\log k/k_0 = \rho\sigma$$

where $k$ is the rate constant of the process, $k_0$ the same constant for the reference compound, $\rho$ the specific rate, and $\sigma$ the electronic contribution from the substituent (*19*).

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 (*20*) in relation to the hydrogenation of ethanol over copper catalysts and has since been studied by a number of authors (*21, 22*).

In this work we studied the reduction of variously substituted acetophenones in order to determine, irrespective of the reaction mechanism involved, whether all arylketones are reduced via a similar reaction pathway over Pd catalysts supported on aluminium orthophosphate and related systems. The solids used in this work ($AlPO_4$ and $AlPO_4$–$SiO_2$) have been employed by Marinas and co-workers since 1970 in different organic processes taking place via carbonium ions (*23*), and later as supports for metals such as Ni, Pd, Pt, and Rh. These catalysts have been applied to the reduction of organic substances such as alkenes (*24*), alkynes (*25*), xylenes (*26*), aromatic nitro compounds (*27*), etc., both by classical hydrogenation and by hydrogen transfer, with excellent results in every case.

## EXPERIMENTAL

### *Supports*

The substances used as supports were pure silica, pure aluminium orthophosphate and mixed 80 : 20 w/w $SiO_2$–$AlPO_4$ systems that were gelled in different media (*28*).

*Synthesis of support F72.* In a 100-ml beaker place 3.56 g of $SiO_2$ (Merck ref. 7734) and 30 ml of distilled water. Then add 3.4 ml of 85% w/w $H_3P_4$ and 1.7 g of $AlCl_3 \cdot 6H_2O$, and stir the mixture for 30 min. Next, immerse the beaker in a bath at 273 K and add 0.1 $M$ $NH_4OH$ dropwise to Ph 6.9. Allow the gel thus formed to stand for 24 h and then filter and air-dry it. Finally, calcine at 923 K for 3 h.

*Synthesis of support F.* Follow the same procedure as for support F72 but using no $SiO_2$.

*Synthesis of support E.* In a 100-ml beaker mix 3.56 mg of $SiO_2$, 30 ml of distilled water, 3.4 ml of 85% w/w $H_3PO_4$ and 1.7 g of $AlCl_3 \cdot 6H_2O$ and stir for 30 min. Then, immerse the beaker in an ice bath and add 50 ml of ethylene oxide in small portions with continuous stirring until a gel is formed. Finally, air-dry and calcine the gel at 923 K for 3 h.

*Synthesis of supports P2 and PM2.* Follow the same procedure as for support E, but replace ethylene oxide with propylene oxide. Wash the solid obtained with isopropyl alcohol ((2 ml $g_{solid}^{-1}$, P2 solid) or ripen with the same alcohol for 15 days (PM2 solid). In either case, calcine the solid at 923 K for 3 h.

The texture and acidity properties of the supports are summarized in Table 1.

The specific surface area of the supports was measured in $m^2/g$. The acidity was determined spectrophotometrically using cyclohexylamine as titrant (*29*). Table 1 gives the amounts of titrant adsorbed as monolayer per gram of solid, $X_m$.

### *Catalysts*

We used Pd systems containing 3% of the metal by weight deposited on the above-mentioned supports. The metal was deposited on the supports by impregnation from aqueous solutions of $5.6 \times 10^{-2}$ *M* $(NH_3)_4PdCl_2$ and subsequent drying in an oven at 383 K for 24 h, after which the system was reduced under a hydrogen stream flowing at a rate of 50 ml/min by raising the temperature to 573 K in a 1 K/min gradient and then keeping it for a further 1 h. The nomenclature of the catalysts denotes the symbol of the metal, that of the support and the percent metal content in each case.

The metal surface area was determined by X-ray diffraction on a Phillips 1130/00/60 instrument using $CuK_\alpha$ radiation with a wavelength of 1.5418 Å and the cubic particle model. The results obtained are listed in Table 2.

### *Catalytic Activity*

Reactions were carried out in a Parr-type hydrogenation reactor furnished with a pressure gauge allowing the hydrogen pressure within the reaction vessel to be measured at any time.

We studied the influence of such factors as the substrate concentration, hydrogen pressure, temperature, and type of catalyst and solvent used on the rate of hydrogenation of acetophenone. For this purpose we used volumes of 20 ml of methanolic solutions of acetophenone at concentrations be-

TABLE 1

Chemical Composition and Properties of the Supports

| Support | Composition | Gelling medium | $S_{BET}$ ($m^2\ g^{-1}$) | Acidity ($X_m \times 10^5$ mol $g^{-1}$) |
|---|---|---|---|---|
| S | Silica gel | Merck ref. 7734 | 412 | 62.0 |
| PM2 | $SiO_2$–$AlPO_4$ (80 : 20) | Propylene oxide | 363 | 60.0 |
| P2 | $SiO_2$–$AlPO_4$ (80 : 20) | Propylene oxide | 458 | 57.0 |
| F72 | $SiO_2$–$AlPO_4$ (80 : 20) | Ammonia | 247 | 40.0 |
| E | $SiO_2$–$AlPO_4$ (80 : 20) | Ethylene oxide | 486 | 20.1 |
| F | $AlPO_4$ | Ammonia | 52 | 32.0 |

TABLE 2

Influence of the Catalyst on the Rate of Hydrogenation of Acetophenone

| Catalyst | $S_{met}$ (m$^2$/g$_{Pd}$) | $r$ (mol$_{H_2}$/s g$_{Pd}$ × 10$^4$) | $r_A$ (mol$_{H_2}$/s m$^2_{Pd}$ × 10$^6$) |
|---|---|---|---|
| PdS–3 | 94 | 1.7 | 1.8 |
| PdPM2–3 | 81 | 4.0 | 5.0 |
| PdF72–3 | 67 | 3.3 | 5.0 |
| PdP2-3 | 66 | 3.1 | 4.7 |
| PdE-3 | 73 | 4.1 | 5.6 |
| PdF-3 | 35 | 6.7 | 19.1 |
| PdAl$_2$O$_3$-5[a] | 111 | 1.1 | 1.0 |
| PdCaCO$_3$-5[b] | 45 | 0.3 | 0.7 |

*Note.* [Subs] = 0.4 *M*, $V_T$ = 20 ml, $T_R$ = 323 K, $P_{H_2}$ = 5 bar, Pd weight = $6 \times 10^{-3}$ g.

[a] Commercially available catalyst (Fluka ref. 76002).

[b] Commercially available catalyst (Fluka ref. 76032).

tween 0.3 and 0.6 *M*. The hydrogen pressure was varied between 3 and 6 bar and the temperature over the range 303–333 K. An amount of metal of $6 \times 10^{-3}$ g was used in every experiment.

The reaction rate was determined from the slope of the hydrogen pressure vs time plot. Blank assays were also run in parallel in order to check that neither the support nor the reactor exerted a catalytic effect. Also, the process was checked not to be controlled by diffusion phenomena under the reaction conditions used. The rate constant per gram of catalyst was found to be constant for amounts of catalyst between 0.05 and 0.5 g, solvent volumes from 10 to 40 ml and grain sizes between 60 and 230 mesh.

### *Product Analysis*

The reaction products were analysed by gas chromatography on a Hewlett–Packard 5830A chromatograph furnished with a 2 m × $\frac{1}{8}''$ column packed with 5% Carbowax on Chromosorb GAW/DMCS. Acetophenone was found to yield 1-phenylethanol and ethylbenzene, while substituted acetophenones yielded the corresponding analogues with unaltered substituents. *p*-Chloroacetophenone yielded a small proportion of the product resulting from the hydrogenolysis of the C–Cl bond. In the presence of two acetyl groups on the ring (1,4-diacetylbenzene), the reduction of the second carbonyl group started only after some *p*-ethylacetophenone was already formed—we only determined the rate of the selective reduction of the first carbonyl group in this case.

## RESULTS AND DISCUSSION

### *Influence of the Catalyst*

Table 2 lists the metal surface area, catalytic activity ($r$) and specific catalytic activity results ($r_A$) obtained in the hydrogenation of acetophenone with catalysts synthesized by the authors and others available commercially and studied for comparison.

The Pd/AlPO$_4$ catalyst proved to be more active than that of Pd/SiO$_2$ and the commercial Pd catalysts, that of Pd/SiO$_2$–AlPO$_4$ yielding intermediate results in this respect. We thus chose catalyst PdF$_3$ (Pd/AlPO$_4$) for subsequent experiments.

### *Influence of the Solvent*

Figure 1 shows the variation of the specific catalytic activity with the dielectric constant of the different solvents assayed for the hydrogenation of acetophenone. We investigated various multiparameter correlations between the reaction rate and the dielectric constant, acidity, basicity, specific gravity, etc., of the solvents used. The best fitting was that between the reaction rate and the dielectric constant of the solvent (Fig. 1): the former decreased with increase in the latter. The influence of the solvent on the rate of many reactions has been studied by a number of authors. Some attribute it to its adsorption into the catalyst sites, where it would compete with substrate (*32*), while others ascribe it to hindered adsorption of the reactions resulting from a major solvation effect arising from a high solvent polarity (*33*). Yet others propose the occurrence of reaction intermediates that are stabilized by the solvent to a varying extent (*34*). The presence of

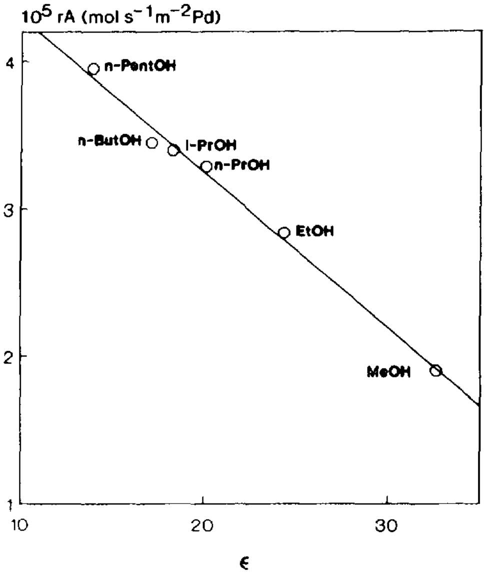

FIG. 1. Variation of the initial rate of acetophenone hydrogenation with the dielectric constant of the solvent.

charged species on the catalyst surface as a result of the addition of hydride ions or protons to the carbonyl group should be more sensitive to the effect of polar solvents than is the hydrogenation by hydrogen atoms via a mechanism of the Horiuti–Polanyi type.

In our case, the hydrogenation of acetophenone does not seem to take place via charged intermediates because the reaction rate is inversely proportional to the dielectric constant of the solvent used. Despite the fact that methanol yields lower rates than do other alcohols, we chose it for all subsequent experiments as it was the only solvent in which all the substituted acetophenones were readily soluble.

### *Reaction Orders*

We studied the reaction rate in relation to the variation of the product distribution with time. By working under reaction conditions similar to those used by Baltzly (*35*), we found the reaction to be of zero-order in the hydrogen pressure and the substrate concentration. In fact, our results conformed to an equation of the type

$$v\ (\text{mmol H}_2/\text{min}) = Akw\theta_H\theta_s,$$

where $A$ is a constant encompassing viscosity, surface tension, and hydrogen solubility factors, $w$ is the catalyst weight used (or its metal surface area), $k$ the hydrogenation constant, and $\theta_H$ and $\theta_s$ the surface fractions covered by hydrogen and the substrate, respectively. This equation only holds provided the overall rate is not controlled by diffusion phenomena. The rate of hydrogen transfer from the gas to the liquid phase was calculated from the intercept of the line obtained by plotting $1/r$ against $1/w$ (Fig. 2), where $r$ is the initial reduction rate of acetophenone in methanol obtained by using different amounts of catalyst, $w$. From the intercept of the plot follows that the rate of hydrogen diffusion is $6.1 \times 10^{-3}$ mol/s and hence much higher than any of the rate values obtained in our experiments for the reduction of acetophenone. Therefore, hydrogen diffusion in methanol can be safely assumed not to affect the rate values obtained in any case.

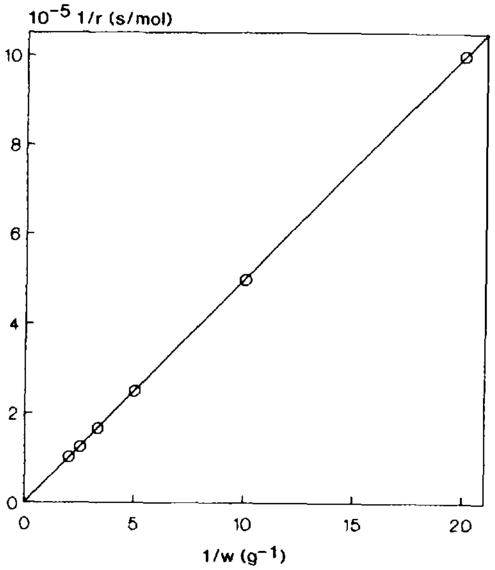

FIG. 2. Variation of the initial rate of acetophenone hydrogenation with the amount of catalyst.

### *Product Distribution as a Function of Time*

Figure 3 shows the variation of the reaction product distribution with time in the form of OPE curves (*36, 37*). According to the reaction profile, the reaction must take place in two steps, namely,

$$C_6H_5COCH_3 \xrightarrow[r_1]{H_2} C_6H_5CHOHCH_3 \xrightarrow[r_2]{H_2} C_6H_5CH_2CH_3.$$

By the time half the hydrogen has been consumed, 1-phenylethanol is the major reaction product; on the other hand, ethylbenzene only begins to be formed in appreciable amounts once all the starting acetophenone has been converted.

From Fig. 3 follows that 1-phenylethanol is an unstable primary product, while ethylbenzene is a stable secondary product. This reaction scheme is different from that proposed by the authors for the hydrogen-transfer reduction of acetophenone using $\alpha$-phellandrene as donor (*38*).

In view of the above reaction scheme and the results shown in Fig. 3, we may state that acetophenone is adsorbed more tightly at the active sites than is 1-phenylethanol, and that only once nearly all acetophenone has reacted does the hydrogenation of 1-phenylethanol to ethylbenzene proceed.

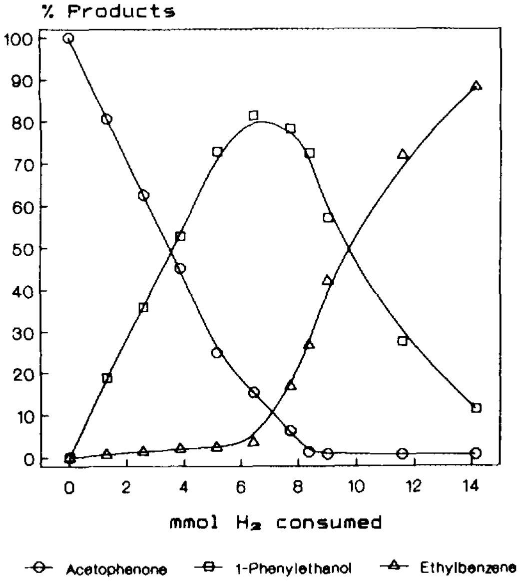

FIG. 3. Variation of the reaction product distribution with the amount of $H_2$ consumed (mmol). Solvent: methanol.

### *Reduction of Enol Ethers*

Aromatic carbonyl compounds are more readily reduced than their nonaromatic counterparts. Thus, acetophenone is more easily reduced that is 2-butanone, whether with dihydrogen of by hydrogen transfer (*38*). According to several authors, the hydrogenation of some carbonyl compounds might involve the enol rather than the keto form of the compound (*39*). With acetophenone, the formation of an ethylene double bond conjugated with aromatic ring might lead one to believe that the equilibrium is more markedly shifted to the enol form than it is for other ketones (e.g., 4-phenyl-2-butanone). This would support the hydrogenation via the enol form. In order to check this point we hydrogenated various compounds with structures similar to that of the enol form of acetophenone. Table 3 lists the results obtained by using the PdF3 system as catalyst. The methyl ether of acetophenone (1-benzylidenyl methyl ether) is reduced 40 times slower than is acetophenone. In order to ascertain that the enolization of acetophenone was not the rate-determining step, we carried out several reactions by using both acetophenone ($r_A = 19.1 \times 10^{-6}$ $\mathrm{mol_{H2}\ s^{-1}\ m_{Pd}^{-2}}$) and deuterated acetophenone ($r_A = 20.1 \times 10^{-6}$ $\mathrm{mol_{H2}\ s^{-1}\ m_{Pd}^{-2}}$) under the same reaction conditions over catalyst PdF3. Keto–enol equilibrium

TABLE 3

Specific Catalytic Activity for the Reduction of Various Substrates

| Substrate | $r_A$ (mol/s $m_{Pd}^2$) × $10^6$ |
|---|---|
| Acetophenone | 19.1 |
| $\alpha$-Methylstyrene | 86.2 |
| 1-Benzylidenyl methyl ether | 0.5 |

*Note.* Conditions as in Table 2.

was reached quite rapidly (somewhat faster for the aldehydes than for the ketones, but subject to a marked isotopic effect in all instances). The similarity between the rates obtained for acetophenone and deuterated acetophenone clearly show that the process is not affected by the concentration of the enol form in the medium and that the reduction process involves the carbonyl group only. Therefore, the hydrogenation of acetophenone does not seem to take place via the ethylene double bond of the enol form, but rather via the carbonyl group directly. In order to check that this was not the result of the steric hindrance posed by the methoxy group, we reacted $\alpha$-methylstyrene under the same conditions. In this case, the reaction rate found was 160 times higher than that of acetophenone methyl ether, so the steric effect of the methoxy group was not indeed responsible for the rate difference between $\alpha$-methylstyrene and the enol methyl ether of acetophenone.

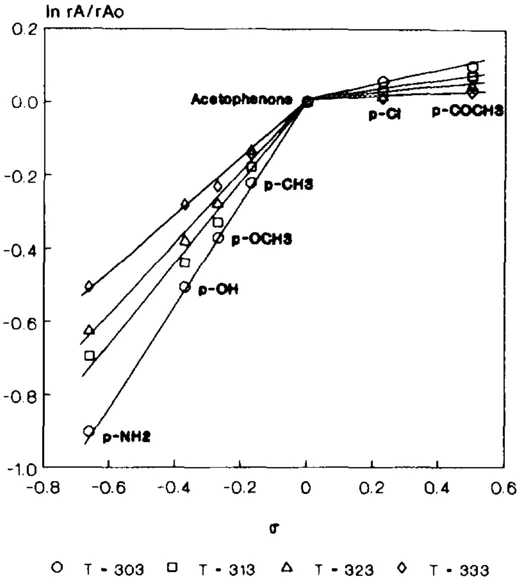

FIG. 4. Hammett plots for the different acetophenones studied.

### *Influence of the Substituents*

In order to determine the effect of substituents of the aromatic ring on the rate of reduction the carbonyl group we reduced variously substituted acetophenones under the same reaction conditions. Figure 4 gives the results obtained at various temperatures. $\sigma^-$ and $\sigma^-$ provided worse fittings. However, the results confirm quite well to the Hammett equation, the curve showing two distinct portions separated by an inflection point for acetophenone. Compounds with electron-withdrawing substituents were reduced faster than those with electron-releasing substituents. However, the fact that they do not fit a single line has been ascribed by some authors (*40*) to the reaction taking place via different pathways depending on the nature of the substituents of the ring. The reaction sensitivity as expressed by $X_m$ was higher for electron-releasing substituents than it was for electron-withdrawing groups (Table 4).

Two-portion Hammett plots are no rare occurrence (*41*, *42*), but are interpreted in rather different ways. Essentially, the process concerned is believed to be affected by the same factors, which, however, are not quantified in the same proportion in dealing with electron-releasing and electron-withdrawing substituents.

In order to check whether the effect of the substituents are always of the same nature (electronic, steric or both), one can seek the occurrence of a compensating effect. By plotting ln $A$ against $E_a$ for the different acetophenones studied we obtained

TABLE 4

$\rho$ Values Obtained in the Hydrogenation of Various Acetophenones

| Temperature (K) | $\rho$ | |
|---|---|---|
| | Electron-releasing substituents | Electron-withdrawing substituents |
| 303 | 1.37 | 0.20 |
| 313 | 1.06 | 0.15 |
| 323 | 0.97 | 0.09 |
| 333 | 0.76 | 0.05 |

an isokinetic temperature $\theta = 378$ K. The good fitting of the results obtained in this respect (Fig. 5) confirms the occurrence of a compensating effect in the process, so we may state that the results obtained for the reduction of the carbonyl group are always influenced by the same type of effect from the substituent, and that the inflection in the Hammett plot arises from the different sensitivity of the reaction for electron-releasing and electron-withdrawing substituents. Despite the fact that the substituents studied were of different size and nature, these two factors do not seemingly contribute to the reaction through secondary effects (steric, adsorptive) other than those resulting from the electron density of the carbonyl group. Otherwise, the plot of ln $A$ vs $E_a$ would not be such a straight line.

In view of the results obtained, the reduction of acetophenones appears to take place via the reaction sequence

$$p\text{-R-C}_6\text{H}_4\text{-CO-CH}_3 \xrightarrow{r_1} p\text{-R-C}_6\text{H}_4\text{-CHOH-CH}_3 \xrightarrow{r_2} p\text{-R-C}_6\text{H}_4\text{-CH}_2\text{-CH}_3,$$

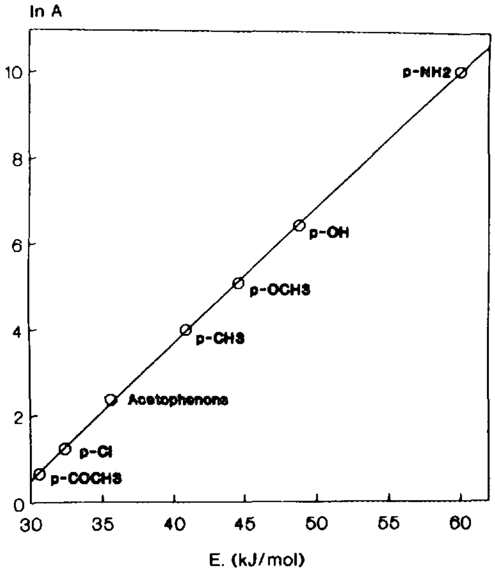

FIG. 5. Compensating effect on the hydrogenation of various acetophenones.

where $r_1 > r_2$ and the process does not involve the enol form. These scheme is similar to those proposed by Bonnet *et al.* (*43*) and Pavlenko (*44*). A more polar solvent would solvate acetophenone to a greater extent, thus hindering its adsorption on the metal. On the other hand, the substituent only appears to have an electronic effect that is transmitted through the aromatic ring and alters the electron density of the carbonyl group. Other secondary effects such as steric effects, adsorptive patterns, etc., resulting from the different nature of the substituents used do not seem to be too influential on the process, and the mechanism via which the acetophenones assayed are reduced is the same in every case.

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