# Transfer of concepts from homogeneous to heterogeneous catalysis: use of Hammett relationships to assess reaction mechanisms and nature of active sites in reactions catalyzed by sulfides, metals, clays and zeolites

A. Finiels, P. Geneste, C. Moreau *

*Laboratoire de Matériaux Catalytiques et Catalyse en Chimie Organique, URA CNRS 418, Ecole Nationale Supérieure de Chimie, 8 Rue Ecole Normale, 34053 Montpellier Cedex 1, France*

## Abstract

The application of Hammett or Hammett-type relationships to a series of various reactions catalyzed by clays, zeolites, sulfides and metals is reviewed in this paper. Such relationships are, of course, of great interest for a better knowledge of the reaction mechanisms over solid catalysts and on the nature of the active species. Among the different data obtained in the laboratory over those catalytic systems, it appears that Hammett slope $\rho$ values for the acid-catalyzed reactions involving Brønsted species in the rate-determining step (hydration, hydrolysis, isomerization, electrophilic aromatic substitution) are of the same order of magnitude for both homogeneous and heterogeneous reactions, whereas deviations are more frequently observed for reactions involving hydrogen.

*Keywords:* Hammett relationships; Mechanisms; Active sites; Sulphides; Metals; Clays; Zeolites

## 1. Introduction

Linear free energy relationships (LFER) are widely used in homogeneously catalyzed reactions to obtain information on both reaction mechanisms and factors affecting the reactivity of organic substrates. Application of such relationships to heterogeneously catalyzed reactions is of particular interest since it is possible to have information on the properties of both organic molecules and solids, in particular from analysis of kinetic and thermodynamic results

that can lead to a better knowledge of the reaction mechanisms over solid catalysts as well as of the nature of the active species.

Since the pioneering reviews on this topic by Kraus [1,2], several authors have attempted to establish that kind of relationships as, for example in our laboratory [3], and more recently, in the carbon–carbon bond formation from metal halides over alkali metal exchanged zeolites [4] or dehydrogenation of alcohols over zinc–chromium oxides [5].

Two types of equations, of the general form: log rate $= \rho\sigma$, in which $\sigma$ is characteristic for the polarity of the substituent and is normally independent of the nature of the reaction, and $\rho$ is characteristic of the reaction and measures the

---

* Corresponding author.

susceptibility of the reaction to polar effects, have been particularly considered: (i) the Taft equation involving polar and steric effects in aliphatic systems, and (ii) the Hammett equation involving polar, resonance and steric effects in aromatic systems, the former aspect being the most often considered. However, Hammett $\sigma$ values measure the resultant of inductive and resonance effects and, in some cases, it was also interesting to consider the Taft's Dual substituent-parameter equation: log rate $= \rho_I\ \sigma_I + \rho_R \sigma_R$ which accounts for the separation of substituent effects into localized (inductive and/or field) and delocalized (resonance) effects [6,7].

All these aspects are being considered in this paper for reactions performed over various catalytic systems such as sulfides, metals, clays and zeolites, important classes of catalysts with respect to their use in refining as well as in organic chemistry.

## 2. Experimental results

### 2.1. Catalysis by sulfides

#### 2.1.1. Hydrogenation and hydrogenolysis of substituted benzenes

In the presence of conventional nickel–molybdenum and cobalt–molybdenum supported hydrotreating catalysts, substituted benzenes undergo at high temperatures and high hydrogen pressure two parallel initial reactions, namely hydrogenolysis of carbon $sp^2$-heteroatom bonds yielding benzene and hydrogenation of the aromatic ring leading to cyclohexane, and it has been previously reported that they are suitable model compounds for evaluating the hydrogenolysis vs. hydrogenation activity of these catalysts [8,9].

#### 2.1.1.1. Hydrogenation of X-substituted benzenes (X = H, SH, $SC_6H_5$, OH, $OC_6H_5$, $NH_2$, $NHC_6H_5$, Cl, Br, F). Experimental results have been accounted for with the Taft's dual-substituent parameter equation: log rate $= \rho_I\ \sigma_I + \rho_R \sigma_R$ in which the contribution of the inductive term is negligible. The substituent constants $\sigma_I$ and $\sigma_R$ are reported in Table 1.

It has been shown that the reaction was mostly influenced by the electron-donating character of the substituents through resonance. The rate of hydrogenation of the benzene ring increases with the increasing electron-donating character of the substituents.

For the hydrogenation reaction of the benzene ring, the negative slope values, $\approx -4$, imply a positively charged transition state and it is now admitted, by analogy with aromatic electrophilic substitution reactions, that a protonic species is transferred from the hydrogenation site to the aromatic ring through formation of a $\pi$-complex [8,10,11].

These results have been confirmed by quantum chemical modelling of the reactivity in which the HOMO levels of the substrates correlate with the hydrogenation rate constants and interact with a protonic (LUMO) catalytic species [12].

More recent results [12] have shown that, at 280°C and 70 bar of hydrogen pressure, unsupported transition metal sulfides, namely Co, Ni, Nb, Mo, Ru, Rh, Pd and W sulfides, behave like their promoted supported counterparts, i.e. the slope values of the correlations found are simi-

Table 1
Inductive ($\sigma_I$) and resonance ($\sigma_R$) substituent constants (data from Ref. [7])

| X | H | SH | SPh | OH | OPh | $NH_2$ | NHPh | Cl | Br | F |
|---|---|----|-----|----|-----|--------|------|----|----|---|
| $\sigma_I$ | 0.00 | 0.27 | 0.31 | 0.24 | 0.40 | 0.17 | 0.30 | 0.47 | 0.47 | 0.50 |
| $\sigma_R$ | 0.00 | −0.17 | −0.13 | −0.42 | −0.34 | −0.47 | −0.50 | −0.21 | −0.19 | −0.33 |

lar, around $-4$. This similar sensitivity to the substituent effects is thus consistent with the existence of a similar active phase in the hydrogenation step.

### 2.1.1.2. Hydrogenolysis of the C–X bond of X-substituted benzenes (X = H, SH, $SC_6H_5$, OH, $OC_6H_5$, $NH_2$, $NHC_6H_5$, Cl, Br, F).

Experimental results have been again accounted for with the same Taft's dual-substituent parameter equation: log rate $= \rho_I \sigma_I + \rho_R \sigma_R$ in which the reaction is mostly influenced by the electron-donating character of the substituents through resonance. The rate of hydrogenolysis of the benzene ring decreases with the increased electron-donating character of the substituents.

For the hydrogenolysis of carbon-substituent bonds, the positive slope values obtained, $+1.9$ for the cobalt promoted catalyst and $+7.5$ for the nickel promoted catalyst, imply a negatively charged transition state, and an analogy with nucleophilic aromatic substitution reactions can be readily considered in which, according to the Pearson's hard and soft acids and bases principle, a soft nucleophilic species like a hydride ion would be the active species [12].

As for the hydrogenation reaction, these results have been confirmed by quantum chemical modelling of the reactivity in which the LUMO levels of the substrates correlate with the hydrogenolysis rate constants and interact with a hydride (HOMO) catalytic species [12].

More recent results obtained over unsupported transition metal sulfides also show positive slope values but they differ to large extent from one catalyst to another. Two distinct groups of data are observed, the first one for metals from groups V and VI with low slope values,

and the second group for metals from groups VIII with higher slope values. Although there is no clear explanation to account for this phenomenon, it seems there might be some relationship with the hard and soft acids and bases (HSAB) principle [13] in relation with the mechanism early proposed by Laine [14] through formation of a complex with metals from group VIII.

All these conclusions are valid providing, of course, the experimental data reflect the surface reaction.

Those conclusions also apply to other organic models in which there is a competition in the initial stage of the reaction between saturation of aromatic rings and cleavage of carbon $sp^2$-heteroatom bonds as, for example, in the benzofurane, benzothiophene and indole series, and in dibenzofurane, dibenzothiophene and carbazole series.

### 2.1.1.3. Hydrogenation of X-substituted benzenes (X = H, $C_2H_5$, $c\text{-}C_6H_{11}$, $c\text{-}C_6H_{11}CH_2$, $C_6H_5$, $C_6H_5CH_2$).

Compared to the preceding series of substituents like heteroatoms or halogens, smaller effects have been obtained with alkyl and aryl groups as substituents. For those compounds for which the electron-donating properties ($\sigma_R$) are roughly similar for all substituents (Table 2), it is then possible to estimate the contribution of the inductive effect.

The higher hydrogenation rate is obtained for the phenyl substituent which has the strongest electron-withdrawing character and only by a factor of 3 [15]. These results are in line with those reported for hydrogenation of methyl-substituted benzenes over $MoS_2$ or $WS_2$ catalysts for which the rate of hydrogenation slightly increases with the increased number of methyl groups [2].

### 2.1.1.4. Hydrogenation of X-substituted thiophenes (X = H, 2-$CH_3$, 3-$CH_3$, 2-$n\text{-}C_4H_9$, 2-$n\text{-}C_8H_{17}$, 2-$C_6H_5$, 3-$C_6H_5$, 2-$C_5H_4N$, 3-$C_5H_4N$).

As for alkyl- and aryl-substituted benzenes, the rates of hydrogenation of thiophenes substituted

Table 2
Inductive ($\sigma_I$) and resonance ($\sigma_R$) substituent constants (data from Ref. [7])

| X | H | $C_2H_5$ | $c\text{-}C_6H_{11}$ | $c\text{-}C_6H_{11}CH_2$ | $C_6H_5$ | $C_6H_5CH_2$ |
|---|---|---|---|---|---|---|
| $\sigma_I$ | 0.00 | $-0.01$ | 0.00 | $-0.03$ | 0.12 | 0.03 |
| $\sigma_R$ | 0.00 | $-0.14$ | $-0.14$ | – | $-0.11$ | $-0.13$ |

at the positions 2 and 3 correlate with the electron-withdrawing properties of the substituents, even with a pyridyl nucleus as substituent [16]. The electron-donating properties of the substituents, $\sigma_R$, are roughly similar for alkyl and pyridyl groups as shown in Table 3.

These results have been again corroborated by a quantum chemical approach of the reactivity and it has been confirmed that the first step in hydroprocessing of thiophene is hydrodearomatization through protonation.

### 2.1.2. Hydrogenation of halonitrobenzenes

Aromatic haloamines are of primary importance in industry for the production of many fine chemicals. They are generally obtained through reduction of the corresponding nitro compounds. Under homogeneous conditions, the reduction by the disulfide $S_2^{2-}$ species gives a positive $\rho$ value of $+3.5$, and it was thus interesting to compare this value with that obtained over conventional hydrotreating sulfided catalysts to know about the active species since it was reported in some papers on the existence of such active species [17].

Over conventional nickel– and cobalt–molybdenum hydrotreating catalysts, only a slight substituent effect is observed, $\rho = +0.4$, with the classical Hammett equation: log rate = $\rho \cdot \sigma_{m,p}$ accounting for the effect of substituents at the meta and para positions. These results would indicate that such a species is not active under heterogeneous conditions and that hydrogen would be only slightly dissociated in the adsorbed transition state [18].

## 2.2. Catalysis by metals

### 2.2.1. Hydrogenation of halonitrobenzenes

This reaction was performed over reduced alumina supported platinum catalysts [19]. As for sulfided catalysts, the effect of substituents on the reactivity of halonitrobenzenes has been measured, and a low positive slope value, $\rho \approx +0.7$ can be deduced from the plot of the logarithms of the rates of hydrogenation against

Table 3
Inductive ($\sigma_I$) and resonance ($\sigma_R$) substituent constants (data from Ref. [7]).

| X | H | CH$_3$ | n-C$_4$H$_9$ | n-C$_8$H$_{17}$ | C$_6$H$_5$ | C$_5$H$_4$N |
|---|------|-------|------|-------|-------|-------|
| $\sigma_I$ | 0.00 | −0.01 | 0.00 | −0.04 | 0.12 | 0.20 |
| $\sigma_R$ | 0.00 | −0.14 | −0.16 | −0.12 | −0.11 | −0.19 |

the substituent constants $\sigma$. A radical mechanism, as already proposed in the literature, or a slight participation of a hydride species resulting from a low dissociation of hydrogen in the adsorbed transition state, can account for the experimental data.

Furthermore it is worth mentioning that the results obtained over metal and sulfided catalysts are roughly similar and are in line with those already reported for the hydrogenation of substituted acetophenones by metal catalysts and for which the slope value is about $\approx +0.7$ whereas reduction by hydride species lead to a higher positive value, $+3.1$ [20].

### 2.2.2. Hydration of benzonitriles

The formation of amides from nitriles is generally known to occur in the presence of acid catalysts but can be strongly accelerated in the presence of copper-based catalysts through formation of more reactive complexes. This is therefore the case for the hydration of acrylonitrile to acrylamide, a reaction of particular industrial interest. The nature of the active copper species is not well known and here again the use of the Hammett relationship is determinant. A low $\rho$ slope value has been obtained, $+0.4$, over Raney copper catalysts, and seems to show the participation of copper as a metal $Cu^0$ instead of a cuprous or cupric species [21].

## 2.3. Catalysis by clays and zeolites

In addition to hydrogenation and hydrogenolysis, acid- and base-catalyzed reactions also constitute an important field of applications in oil refining as well as in organic chemistry, particularly for the substitution of homogeneous

by heterogeneous catalysts in order to overpass technical and environmental drawbacks and facilitate the easier recovery of the products.

### 2.3.1. Hydrolysis of acetals

The first reaction considered in the laboratory was the hydrolysis of acetals, a reaction well known to give easily a quantitative measure of the protonic activity under homogeneous conditions, and that might constitute a kinetic tool to determine the effective acidity of solid catalysts under heterogeneous working conditions, particularly when solvents are used [3].

Apart from the determination of a scale of acidity for different clays and zeolites in water, it was also shown that the reaction mechanism was closely similar to that working in solution. Hammett $\rho$ values of $-2.7$ and $-3.2$ have been obtained over H-montmorillonite K10 and H-MOR (Si/Al = 6.9) respectively and are of the same order of magnitude as that obtained in solution, $-3.3$ [22].

### 2.3.2. Acylation of aromatic compounds

The Friedel–Crafts reaction was first investigated on the basis of more friendly environmental considerations, i.e. to replace aluminum chloride by solid catalysts and to avoid the presence of chlorine atoms in the effluents by using directly carboxylic acids instead of acyl chlorides [23]. It has been effectively shown that carboxylic acids replace advantageously the corresponding acyl chlorides and that zeolites also replace advantageously aluminum chloride. Moreover, the utilization of zeolites generally increases the selectivity toward para isomers, as due to the shape selective properties of that class of catalysts.

Concerning the effect of substituents on the acylation reaction of substituted benzenes with octanoic acid, a Hammett $\rho$ value of $-5$ has been found which is comparable to the value of $-7$ obtained in the AlCl$_3$-catalyzed reaction, thus confirming the attack of the electrophilic species RCO$^+$, previously formed in a fast step, on the aromatic ring. The slightly smaller $\rho$

value could result from a better stabilization of the transition state over the solid.

When the acylating reagent is itself substituted as for example in the acylation of thiophene with para-substituted benzoyl chlorides, no effect of substituent is observed, $\rho = -0.3$, thus confirming the formation of the acylium species in a first and fast step [24].

### 2.3.3. Hydration of aromatic acetylenics and nitriles

Following the same approach of the replacement of homogeneous by heterogeneous catalysts, hydration of acetylenics has been considered as, for example, in the hydration of phenylacetylene over a H-Y-FAU (Si/Al = 15) catalyst at 150°C. The formation of a carbocationic species in the rate-determining step is likely to occur as hydration is favored by electron-donating substituents. A negative Hammett $\rho$ value, $-2.7$, indicative of a positively charged transition state, is obtained [25]. As for other preceding reactions catalyzed by zeolites or clays, the $\rho$ value is slightly smaller than that determined in homogeneous medium, $-3.8$, which can be explained by a better stabilization of the transition state through adsorption.

Hydration of aromatic nitriles was also investigated in the presence of acidic zeolites [26]. The hydration of substituted benzonitriles was performed on a slightly acidic H-Y-FAU (Si/Al = 2.5) zeolite at 250°C in water/ethanol mixtures. The course of the reaction is more complex since it involves several steps catalyzed by acids and bases. The absence of substituent effects seems to show that the electron-donating properties of the substituents would favor the heterolysis of the CN triple bond but would hinder the formation of the new bond with the nucleophile. A concerted mechanism is thus proposed in which the nucleophilic attack by water on the protonated nitrile competes with the deprotonation of the resulting adduct by another water molecule. This proposal agrees with the mechanism of acid-catalyzed hydration of nitriles in homogeneous conditions and con-

firms that the rate-determining step is different from that observed in hydration of CC triple bonds.

### 2.3.4. Isomerization of substituted halobenzenes

Isomerization of halobenzenes, bromobenzenes and fluorobenzenes substituted by $CH_3$, F, Cl, Br and I groups, was performed in the gas phase over a wide pore H-BEA (Si/Al = 8) zeolite, at temperatures ranging from 250°C to 330°C and a partial pressure of 133 Pa [27]. As for other reactions involving a protonic species in the rate-determining step, a negative Hammett $\rho$ value, $-3.4$, has been obtained. This suggests the formation of a protonated intermediate through splitting of the aryl–halogen bond, in agreement with the mechanism already proposed for the $AlCl_3$-catalyzed reaction. Confirmation of the presence of protonated species at the surface of the catalyst was also shown by studies of the adsorbed phase by $C^{13}$ MAS NMR and FTIR.

### 2.3.5. Nitration of aromatics

Nitration is one of the most important among electrophilic aromatic substitution reactions and various solid catalysts have already been proposed to replace the conventional sulfonitric mixture.

Vapor phase nitration of aromatics can proceed through different mechanisms involving free radical, cationic or radical cationic species. The formation of organic radical cations is already known over solid catalysts and substituent effects are normally expected to confirm, or not, the validity of this hypothesis which is a matter of controversy. In order to get more information on the nature of the active species, the vapor phase nitration of benzenes substituted by fluorine, chlorine and trifluoromethyl groups was performed over a H-BEA (Si/Al = 27) zeolite at 140°C and atmospheric pressure with dinitrogen tetroxide [28].

From the plots of the logarithms of the partial rate factors against the substituent constant $\sigma^+$, the Hammett correlation is poor even after mod-

ifications of the kind proposed by Yukawa and Tsuno. Thus the activity is not satisfactorily correlated with an electrophilic mechanism involving an aromatic cationic species. Moreover, from the product distribution a mechanism involving a free radical species was also readily ruled out. Finally, a better correlation was found by plotting the initial reaction rates against the ionization potentials of the aromatic compounds, thus favoring the formation of an aromatic radical cation species in the rate-determining step.

### 2.3.6. Condensation of aldehydes with ketones

Up to now most of the correlations were examined for hydrogenation and acid-catalyzed reactions over solid catalysts. This is mainly due to the numerous applications in oil refining. As a consequence, the development of heterogeneous catalysis by solid bases is more recent and mainly concerned with applications in organic chemistry, i.e. the replacement of liquid bases like NaOH or KOH by their solid counterparts.

Among the different classes of solid bases, hydrotalcites appeared to have high basic properties. Hydrotalcites were synthesized with Mg/Al atomic ratios of 2.5 and 3, and with different contents of exchangeable $Cl^-$ and $CO_3^{2-}$ anions. They contain basic sites with $pK_a$'s ranging from 10.7 to 13.3 with a few sites with a $pK_a$ of 16.5.

The activity of such basic catalysts was tested in the Claisen–Schmidt condensation reaction of substituted benzaldehydes with acetone at 110°C under nitrogen pressure [29]. According to the mechanism operating in solution, the first step of the condensation between benzaldehyde and acetone would be the abstraction of a proton from acetone by the basic sites of the solid. This hypothesis is easily confirmed by performing the reaction with substituted benzaldehydes. A linear Hammett correlation was found when plotting the logarithms of the rate constants against the substituent constants $\sigma^+$. The slightly positive $\rho$ value, $+0.7$, is of the same magni-

tude as those found for NaOH and $Al_2O_3$ catalysts. The rate-determining step would thus imply the nucleophilic addition of a carbanion species $^-CH_2$–CO–$CH_3$ to the carbonyl group of the benzaldehyde.

## 3. Conclusions

Providing the experimental data reflect the surface reaction, all the results reported in this paper, covering a wide range of fundamental organic reactions like hydrogenation, acid- and base-catalyzed reactions, show that the use of Hammett relationships is a remarkable tool in order to obtain information on reaction mechanisms over solid catalysts and on the nature of the active sites.

Reaction mechanisms of heterogeneously catalyzed reactions generally parallel those for the homogeneously catalyzed reactions for reactions catalyzed by acids and bases, whereas some deviations are observed for reactions involving hydrogen. In this latter case, it is then possible to distinguish between hydrogen molecules bonded to the catalyst surface and hydrogen molecules dissociated into hydride and proton species. Molecular orbital calculations and quantum chemical modelling of the reactivity and the nature of active sites, also constitute an additional tool to assess reaction mechanisms.

## Acknowledgements

## References

[1] W. Kraus, Adv. Catal., 17 (1967) 75.
[2] W. Kraus, Adv. Catal., 29 (1980) 151.
[3] B. Coq, R. Durand, F. Fajula, C. Moreau, A. Finiels, B. Chiche, F. Figueras and P. Geneste, Stud. Surf. Sci. Catal., 41 (1988) 241.
[4] D.K. Murray, J.W. Chang and J.F. Haw, J. Am. Chem. Soc., 115 (1993) 4732.
[5] D. Gulkova and W. Kraus, J. Mol. Catal., 87 (1994) 47.
[6] J. Shorter, in N.B. Chapman and J. Shorter (Eds.), Correlation Analysis in Chemistry: Recent Advances, Plenum Press, New York, 1978, p. 119.
[7] M. Charton, Prog. Phys. Org. Chem., 13 (1981) 119.
[8] C. Moreau, C. Aubert, R. Durand, N. Zmimita and P. Geneste, Catal. Today, 4 (1988) 117.
[9] C. Moreau, J. Joffre, C. Saenz and P. Geneste, J.Catal., 122 (1990) 448.
[10] B.S. Gevert, J.E. Ottersted and F.E. Massoth, Appl. Catal., 31 (1987) 113.
[11] J. Joffre, P. Geneste, J.B. Mensah and C. Moreau, Bull. Soc. Chim. Belg., 100 (1991) 865.
[12] C. Moreau, J. Joffre, C. Saenz, J.C. Afonso and J.L. Portefaix, Proc. 13th Iberoamerican Symp. Catalysis, Segovia, 1992, p. 1162.
[13] R.G. Pearson, J. Am. Chem. Soc., 85 (1963) 3533.
[14] R.M. Laine, New J. Chem., 11 (1987) 543.
[15] C. Aubert, R. Durand, P. Geneste and C. Moreau, J. Catal., 112 (1988) 12.
[16] J. Joffre, P. Geneste, A. Messalhi, C. Moreau and J.L. Olivé, unpublished results.
[17] M. Vrinat, C. Guillard, M. Lacroix, M. Breysse, M. Kurdi and M. Danot, Bull. Soc. Chim. Belg., 96 (1987) 1017.
[18] C. Moreau, C. Saenz, P. Geneste, M. Breysse and M. Lacroix, Stud. Surf. Sci. Catal., 59 (1991) 121.
[19] B. Coq, A. Tijani and F. Figueras, J. Mol. Catal., 68 (1991) 331.
[20] H. Van Bekkum, A.P. G. Kieboom and K.J. Van De Putte, Recl. Trav. Chim. Pays-Bas, 88 (1969) 52.
[21] S. Mseddi, F. Figueras, C. Moreau and R. Pich, Proc. 1st French–Maghreb Colloquium on Catalysis, Hammamet, 1990 (Publ. 1993) p. 313.
[22] R. Durand, P. Geneste, C. Moreau and S. Mseddi, Stud. Surf. Sci. Catal., 20 (1985) 319.
[23] B. Chiche, A. Finiels, C. Gauthier and P. Geneste, Appl. Catal., 30 (1987) 365.
[24] A. Finiels, A. Calmettes, P. Geneste and P. Moreau, Stud. Surf. Sci. Catal., 78 (1993) 595.
[25] A. Finiels, F. Marichez, P. Geneste and P. Moreau, unpublished results.
[26] M. Laspéras, P. Graffin and P. Geneste, J. Catal., 139 (1993) 362.
[27] B. Coq, J. Pardillos and F. Figueras, Stud. Surf. Sci. Catal., 59 (1991) 581.
[28] A. Germain, T. Akouz and F. Figueras, J. Catal., 147 (1994) 163.
[29] D. Tichit, M.H. Lhouty, A. Guida, B. Chiche, F. Figueras, A. Auroux, D. Bartalini and E. Garrone, J. Catal., 151 (1995) 50.