in tetrahydrofuran (16 mL) according to the literature method,[5a,d] was added the phosphate **9** (1.62 g, 5.1 mmol) at −78 °C, and the mixture was stirred for 20 min at −78 °C and then 1 h at room temperature. The solvent was removed under reduced pressure, and the residue was washed several times with ether. The ether washings were dried over Na_2SO_4 and then column chromatographed on alumina (pentane–ether, 10:1) under nitrogen atmosphere. A yellow band was collected, and the solvent was evaporated to give yellow crystals of iron complex **10** (907 mg, 57%), mp 62–64 °C. The spectral data of this compound and other (η^1-allyl)Fp complexes (**3a–f**) are summarized in Table II in the supplementary material.

Protonation of (η^1-Allyl)Fp Complexes. Synthesis of (η^2-olefin)$Fp^+BF_4^-$ **4a–e** and **11**. The following reaction of **10** is representative. Complex **10** (421 mg, 1.35 mmol) was dissolved in a mixture of methanol (3 mL) and dichloromethane (3 mL). Tetrafluoroboric acid (42%, 0.22 mL, 1.62 mmol) diluted with methanol (1 mL) and dichloromethane (1 mL) was added over a period of 30 min, and the mixture was stirred for 2 h. Ice-water (30 mL) was added, and the mixture was extracted with dichloromethane. Dried over Na_2SO_4, the solvent was evaporated under reduced pressure to give a yellow solid. Recrystallization from dichloromethane–ether gave a yellow needles of complex **11** in quantitative yield. The melting points and the analytical and the spectral data of **11** and other (η^2-olefin)Fp cations **4a–e** are listed in Tables III and IV in the supplementary material.

Reaction of (η^2-β-Pinene)Fp^+ BF_4^- (11) with Sodium Iodide. To a solution of the cationic complex **11** (902 mg, 2.25 mmol) in acetone (18 mL) was added sodium iodide (405 mg, 2.7 mmol), and the mixture was stirred for 2 h in an ice bath. The solvent was then removed, and the black residue was chromatographed on silica gel with pentane as an eluate to give β-pinene in 52% yield. The product was identical (GLC and ^1H NMR) with an authentic sample obtained commercially.

Registry No. **2a**, 83036-58-2; **2b**, 83036-59-3; **2c**, 101494-37-5; **2d**, 101494-38-6; **2e**, 101494-39-7; **2f**, 101494-40-0; **3a**, 38905-70-3; **3b**, 101494-26-2; **3c**, 101494-27-3; **3d**, 56389-66-3; **3e**, 101494-28-4; **3f**, 101494-29-5; **4a**, 89043-54-9; **4b**, 101494-31-9; **4c**, 101494-33-1; **4d**, 59980-55-1; **4e**, 101517-38-8; **6**, 80-56-8; **7**, 127-91-3; **8**, 515-00-4; **9**, 101494-41-1; **10**, 101494-34-2; **11**, 101494-36-4; $NaFe(CO)_2Cp$, 12152-20-4; $ClP(O)(O\text{-}i\text{-}Pr)_2$, 2574-25-5; 3,7-dimethyl-1,6-octadiene, 2436-90-0.

Supplementary Material Available: Physical properties, spectral data, and analyses for compounds prepared (6 pages). Ordering information is given on any current masthead page.

Friedel–Crafts Acylation of Toluene and *p*-Xylene with Carboxylic Acids Catalyzed by Zeolites

Bich Chiche, Annie Finiels, Catherine Gauthier, and
Patrick Geneste*

*Laboratoire de Chimie Organique Physique et Cinétique
Chimique Appliquées, UA 418, Ecole Nationale Supérieure
de Chimie de Montpellier 8, rue Ecole Normale, 34075
Montpellier Cedex, France*

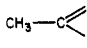
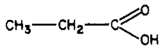
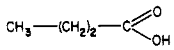
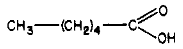
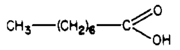
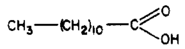
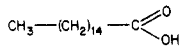
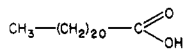
Jean Graille and Daniel Pioch

*Division Chimie des Corps Gras, CIRAD-IRHO, BP 5035,
34032 Montpellier Cedex, France*

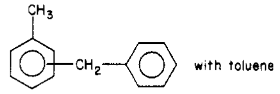
Received July 16, 1985

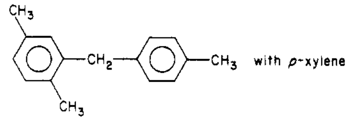
The Friedel–Crafts reaction (alkylation and acylation of aromatic compounds) has been extensively studied in the past over various Lewis acid catalysts ($AlCl_3$, $FeCl_3$, $TiCl_4$)[1] and protonic acids (HF, H_2SO_4, HCl). Zeolites have received much attention recently in a wide range of contexts, particularly in the area of catalysis.[2] However, little attention has been given to the possibility of employing zeolites for promoting the Friedel–Crafts reaction.

Table I. Acylation of Toluene and *p*-Xylene by Carboxylic Acids[a]

	aromatic compound				
	toluene				*p*-xylene
acylating agent	% yield (±2%) in acylated product[b]	isomers ortho	meta	para	% yield (±2%) in acylated product[b]
acetic acid  $CH_3—C(=O)OH$	ϵ[c]				ϵ[c]
propionic acid  $CH_3—CH_2—C(=O)OH$	6	3	2	95	8
butyric acid  $CH_3—(CH_2)_2—C(=O)OH$	20	3	2	95	22
hexanoic acid  $CH_3—(CH_2)_4—C(=O)OH$	30	3	3	94	40
octanoic acid  $CH_3—(CH_2)_6—C(=O)OH$	75	3	3	94	80
dodecanoic acid  $CH_3—(CH_2)_{10}—C(=O)OH$	96	3	3	94	93
palmitic acid  $CH_3—(CH_2)_{14}—C(=O)OH$	80	0.5	1	98.5	97
behenic acid  $CH_3—(CH_2)_{20}—C(=O)OH$	55	0	0	100	60

[a] Conditions: see Experimental Section. [b] As expected, it was found that a secondary product, at a very low yield <1%, was formed, with toluene as well as with *p*-xylene, which results from dismutation of methyl benzenes.[8] ^{13}C NMR has provided convincing evidence for the structure assigned:





[c] It was verified that no side reaction occurs when the acylation reaction takes place partially, except the dismutation of methyl benzenes (see fnt *b*); the unreacting starting materials are fully recovered.

Zeolites are salts of solid silicoaluminic acids characterized by a strictly regular structure of their crystalline lattice[3] and belonging to acid-type catalysts.[4] The acid form of zeolites is important in a variety of catalytic reactions including hydrocarbon cracking,[5] isomerization,[6] and alkylation.[7] These organic processes have been the subject of considerable interest during the last decade.

The present paper is concerned with the catalytic acylation of toluene and *p*-xylene by different carboxylic acids

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[1] Olah, G. A. *Friedel–Crafts and Related Reactions*: Wiley-Interscience: New York and London, 1963–1964; Vol. I–IV.

[2] (a) Venuto, P. B.; Landis, P. S. *Adv. Catal.* **1968**, *18*, 346. (b) Venuto, P. B. *Adv. Chem. Ser.* **1971**, *102*, 260.

[3] (a) Breck, D. W. *Zeolite Molecular Sieves*, Wiley: New York, 1974. (b) Rabo, J. A. *Zeolite Chemistry and Catalysis*; ACS Monograph 171, American Chemical Society, Washington, D.C., 1976.

[4] Figueras, F., personal communication, 1984.

[5] Oblad, A. G. *Oil Gas J.* **1972**, *70*(13), 84.

[6] Benesi, H. A. *J. Catal.* **1967**, *8*, 368.

[7] (a) Venuto, P. B.; Hamilton, L. A.; Landis, P. S.; Wise, J. J. *J. Catal.* **1966**, *5*, 81. (b) Daage, M.; Fajula, F. *Bull Soc. Chim. Fr.* **1984**, *5*, 153 and 160.

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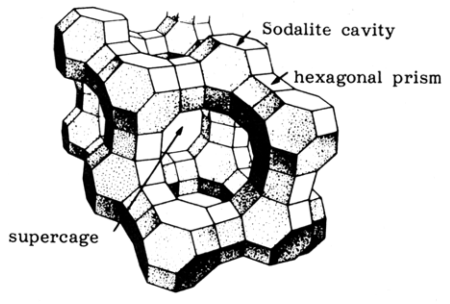
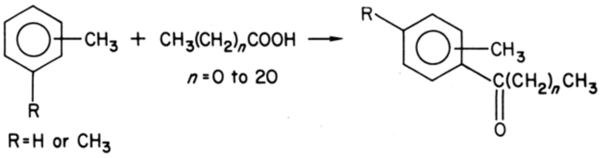


Figure 1. Faujasite-type zeolite framework.

over a Y-type zeolite (eq 1), particularly by using long chain fatty acids. So far, the best catalyst was found to be a Y-faujasite-type zeolite ($Na_{56}(AlO_2)_{56}(SiO_2)_{136}\cdot nH_2O$) exchanged with Ce^{3+} cation. As shown in Figure 1, the faujasite-type framework is composed of a system of cavities. The largest cavity "supercage" has a free diameter of about 12 Å and a 12-oxygen window of 7 Å^3. The CeY zeolite exhibits high activity in other organic reactions such as alkylation.[8] Table I gives a summary of results.



(1)

It can be noted that, with fatty acids ($n > 6$), the acylation of aromatic compounds takes place with yields higher than 50%. But the most interesting feature is the excellent selectivity found in the acylation of toluene where, with all acids studied, the yield of para isomer was at least 94%. In classical Friedel–Crafts acylations, generally predominant para substitution is observed.[9] The mechanism has been studied by using the Brown selectivity relationship which predicts that substrate and positional selectivity both increase as the reactivity of the electrophile decreases.[10]

In this study, the acylation of toluene and benzene with octanoic acid catalyzed by the CeNaY zeolite shows low K_T/K_B rate ratio (K_T/K_B obtained by the competitive method of rate determination = 12) and high para/ortho isomer ratio (94% para isomer), i.e., low substrate but high positional selectivities. These observations are inconsistent with the Brown selectivity rules which predict that low substrate selectivity is accompanied by little discrimination between available positions.

In order to compare this new process with classical Friedel–Crafts acylation, we have studied the acylation of benzene and toluene with $AlCl_3$. Under these conditions, the K_T/K_B value for octanoic acid (= 10) is in good agreement with that obtained with the CeNaY zeolite. However, the yield of para isomer is not as high (79%), due to the increasing percent of ortho.

The high positional selectivity observed in these zeolite catalyzed electrophilic aromatic substitutions can be explained by invoking the shape-selectivity of zeolites which is due to the shape of the channels: the ortho isomer might not be formed due to a lack of space within the channel or cavity. Extension of this concept to the various substrates is currently under study in order to explain the mechanism of acylation catalyzed by zeolites.

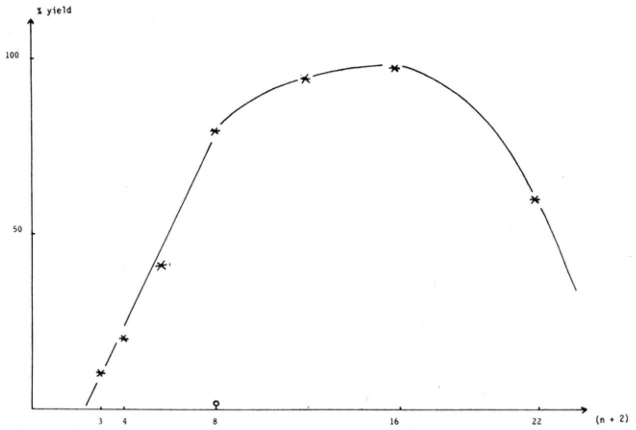


Figure 2. Percent yield vs. the number ($n + 2$) of carbon atoms of carboxylic acids.

In the acylation of p-xylene, a plot of percent yield as a function of the number ($n + 2$) of carbon atoms of carboxylic acids gives the graph in Figure 2. The maximum yield was obtained for acids from C_{12} to C_{20}. For longer chains, the yield decreases. This observation suggests that the large substrates cannot penetrate the cavities and consequently cannot interact with the active site; consequently it may be reasonably supposed that the reaction is intracrystalline, i.e., inside the porous network instead of only on the surface. This type of shape-selectivity is in connection with the sieving properties of zeolites.

For short alkyl chain acids, as seen in Figure 2, we obtain a straight line. Although the molecules are able to diffuse through the porous network, the yield increases linearly as the hydrocarbon chain is lengthened. This phenomenon is not encountered in classical Friedel–Crafts reactions and is not clearly understood as yet but it is probably due to the same reason as previously mentioned, i.e., intracrystalline reaction. Such a behavior due to hydrophobic interactions between the surfactant and the hydrocarbon chain of the substrat has been noted in micellar catalysis.[11]

Investigations are being performed to gain further understanding of the catalysis by zeolites, for example, by using other solids with smaller pores such as mordenite and ZSM-5 zeolite, exchanged with different cations.

Experimental Section

Analyses were performed on a gas chromatograph equipped with flame ionization detector and using a 5% FFAP column (2 m × $^1/_8$ in. Chromosorb WAW, DMCS, 80–100 mesh). The ^1H NMR spectra were taken with a Bruker WP 60 CW spectrometer. The ^{13}C NMR spectra were measured in $CDCl_3$ solution on a Bruker WP 80 spectrometer. GLC–mass spectral analyses were performed on a Hewlett-Packard Model 5890 using a OV1 capillary column (10 m) which was coupled to a MS-5970 A mass spectrometer and a 2671 G Data System.

Materials. All starting materials were pure grade samples supplied primarily by Fluka or Aldrich. The NaY zeolite was supplied by Linde Division, Union Carbide.

CeY zeolite was prepared by conventional ion exchange (24 h–room temperature) of NaY with 1 M aqueous $Ce(NO_3)_3$ solutions. The solid was then thoroughly washed and dried at 80 °C. The level of ion exchange, as determined by microanalysis was 70% of that theoretically possible, indicating essentially complete replacement of Na^+ ions in accessible sites. X-ray diffractograms indicated that no loss of structure resulted from the exchange process. The catalyst was calcined overnight at 500 °C, in air, prior to use. After the acylation, it was verified that the zeolite was still crystalline.

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[8] (a) Gnep, N. S.; Tejada, J.; Guisnet, M. *Bull. Soc. Chim. Fr.* **1982**, *1*, 5. (b) Harbison, K. G. *J. Chem. Educ.* **1970**, *47*, 837.

[9] Jensen, F. F.; Goodman, G. In *Friedel–Crafts and Related Reactions*; Olah, G. A., Ed.; Wiley-Interscience: New York and London, 1964; Vol. III, Part 2, pp 1024–1032.

[10] Stock, L. M.; Brown, H. C. *Adv. Phys. Org. Chem.* **1963**, *1*, 35.

[11] Finiels, A.; Geneste, P. *J. Org. Chem.* **1979**, *44*, 2036.

General Procedure. The reactions were carried out in a 0.1-L stirred autoclave (Sotelem) operating in a batch mode and equipped with a system for sampling of liquid during the course of the reaction.

The experimental procedure was as follows. The autoclave was charged with the freshly calcined zeolite (500 mg) or $AlCl_3$ (1 g) and the carboxylic acid (**1**, 5×10^{-3} mol) together with the aromatic compound (50 cm^3) and heated at 150 °C during 48 h. Under these conditions, the reactions follow pseudo-first-order kinetics. The products isolated by column chromatography on alumina with cyclohexane/ether (95:5) as eluent were identified by ^{13}C and ^{1}H NMR and by GLC–mass spectrography.

For competitive reactions, the autoclave was charged as previously described, using a mixture of benzene and toluene (50:50) as solvent. Samples were withdrawn periodically and analysed with gas–liquid chromatography. Relative rate constants can be determined by measuring the relative concentrations of the products. It was verified that the concentrations of products were in a constant ratio, independent of time.

Registry No. PhMe, 108-88-3; p-$Me_2C_6H_4$, 106-42-3; CH_3CO_2H, 64-19-7; $CH_3CH_2CO_2H$, 79-09-4; $CH_3(CH_2)_2CO_2H$, 107-92-6; $CH_3(CH_2)_4CO_2H$, 142-62-1; $CH_3(CH_2)_6CO_2H$, 124-07-2; $CH_3(CH_2)_{10}CO_2H$, 143-07-7; $CH_3(CH_2)_{14}CO_2H$, 57-10-3; $CH_3(CH_2)_{20}CO_2H$, 112-85-6; $CH_3C(O)$-p-C_6H_4Me, 122-00-9; $CH_3CH_2C(O)$-p-C_6H_4Me, 5337-93-9; $CH_3(CH_2)_2C(O)$-p-C_6H_4Me, 4160-52-5; $CH_3(CH_2)_4C(O)$-p-C_6H_4Me, 1669-33-6; $CH_3(CH_2)_6C(O)$-p-C_6H_4Me, 51770-83-3; $CH_3(CH_2)_{10}C(O)$-p-C_6H_4Me, 50671-19-7; $CH_3(CH_2)_{14}C(O)$-p-C_6H_4Me, 2657-10-5; $CH_3(CH_2)_{20}C(O)$-p-C_6H_4Me, 101493-90-7; 1-(2,5-dimethylphenyl)ethanone, 2142-73-6; 1-(2,5-dimethylphenyl)-1-propanone, 35031-52-8; 1-(2,5-dimethylphenyl)-1-butanone, 35031-53-9; 1-(2,5-dimethylphenyl)-1-hexanone, 17424-48-5; 1-(2,5-dimethylphenyl)-1-octanone, 101493-87-2; 1-(2,5-dimethylphenyl)-1-dodecanone, 101493-88-3; 1-(2,5-dimethylphenyl)-1-hexadecanone, 101493-89-4; 1-(2,5-dimethylphenyl)-1-docosanone, 101493-91-8.

Linear Solvation Energy Relationships. 40. A Reexamination of ^{13}C NMR Shifts and ^{13}C–^{19}F Coupling Constants of Trifluoroacetic Acid Complexes with Hydrogen Bond Acceptor Bases

Mikael Begtrup,* Robert W. Taft,* and Mortimer J. Kamlet*

Department of Organic Chemistry, The Technical University of Denmark, DK-2800 Lyngby, Denmark, Department of Chemistry, University of California, Irvine, California 92717, and Naval Surface Weapons Center, White Oak Laboratory, Silver Spring, Maryland 20910

Received October 29, 1985

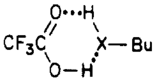
One of us has recently reported[1] an analysis of NMR spectral data of complexes of trifluoroacetic acid with hydrogen bond acceptor bases in CCl_4. ^{13}C Shifts of the carbonyl and CF_3 carbons and $^{1}J_{CF}$ and $^{2}J_{CF}$ coupling constants were determined for a number of n-butyl derivatives, n-BuX (X = Cl, CH=CH$_2$, CH=O, OH, SH, COOH, NO_2, etc.), and rationalized in terms of *linear solvation energy relationships* of the form of eq 1. The

$$XYZ = XYZ_0 + s\pi^* + a\alpha + b\beta + e\xi \qquad (1)$$

π^*, α, and β terms in eq 1 are the *solvatochromic parameters* that measure molecular dipolarity/polarizability, HBD (hydrogen bond donor) acidity, and HBA (hydrogen bond acceptor) basicity.[2] The ξ term is a *coordinate covalency* parameter[3] that has been used in conjunction with the β parameter to correlate and rationalize certain "family-dependent" basicity properties, i.e., properties (like aqueous pK_a) that are linear with β within families of bases having similar HBA sites (double-bonded oxygen bases, single-bonded oxygen bases, pyridine bases, sp^3-bybridized amine bases) but not between families. The equations of the form of eq 1 were then used to estimate new β_i values which were averaged to arrive at β values for some additional n-BuX derivatives. The β_i values from the different equations showed only modest agreement with one another and with β values estimated earlier by other methods.[2]

At the time the paper dealing with the $CF_3COOH{\cdot}HBA$ complexes appeared,[1] there were in the press three papers, coauthored by the other authors of the present paper,[3–5] that had a direct bearing on this study in a number of regards. (a) First, it was shown[3] that NMR shifts of HBA base complexes with trifluoroethanol, 4-fluorophenol, and 5-fluoroindole are family-independent properties, which are linear with β for all types of HBA bases without the intervention of the ξ parameter. The same is likely to be true of CF_3COOH complexes. (b) More importantly, it was also shown[4,5] that π^*, α, and β values of amphihydrogen bonding compounds are different depending on whether they are self-associated solvents or non-self-associated "monomer" solutes in dilute solutions. Thus, the π^* and β values of n-BuOH solvent are 0.47 and 0.88,[2] whereas the "monomer" π^*_m and β_m values are 0.40 and 0.45.[4] Under the conditions of the measurements discussed here (1.0 M CF_3COOH and 1.0 M HBA base in CCl_4), however, the n-BuX compounds, where X = OH, COOH, and SH, are unlikely to be either fully dissociated, as in more dilute solutions, or as fully associated as in the neat solvents. It would follow, therefore, that neither the π^*, α, and β nor the π^*_m, α_m, and β_m parameters are completely appropriate to describe the properties of the complexes with these amphihydrogen bonding solutes. (c) Finally, from solubility data in water and from octanol/water partition coefficients, we have been able to estimate[4] a number of additional β values which are germane to the present study.

Even if the NMR studies had been carried out at solute concentrations sufficiently low that the amphihydrogen bonding compounds would be "monomeric", another effect, not addressed in sufficient detail in any of our earlier LSER papers, would be likely to further complicate the correlations. This involves the likelihood of type AB hydrogen bonding, wherein both species involved act simultaneously as both HBD acids and HBA bases in a probably cyclic complex.[6] For n-BuXH and CF_3COOH, type AB hydrogen bonding would be represented by I. Strengths and effects of type AB hydrogen bonds are generally different than would be predicted from the summation of $a\alpha$ and $b\beta$ terms in eq 1.



I, X = O, S

For the above reasons we have now combined our efforts in order to reexamine and reinterpret the results of the NMR studies. Data for n-BuX compounds for which the solvatochromic parameters are known or can be estimated reliably (from corresponding values for closely related compounds), but excluding the results for X = OH, SH,

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(1) Begtrup, M. *Acta Chem. Scand., Ser. A* **1985**, *A39*, 117.

(2) Kamlet, M. J.; Abboud, J.-L. M.; Abraham, M. H.; Taft, R. W. *J. Org. Chem.* **1983**, *48*, 2877.

(3) Kamlet, M. J.; Gal, J. F.; Maria, P. C.; Taft, R. W. *J. Chem. Soc., Perkin Trans. 2*, in press.

(4) Taft, R. W.; Abraham, M. H.; Doherty, R. M.; Kamlet, M. J. *Nature (London)* **1985**, *313*, 384.

(5) Kamlet, M. J.; Abraham, M. H.; Doherty, R. M.; Taft, R. W. *J. Am. Chem. Soc.* **1984**, *106*, 461. Taft, R. W.; Abraham, M. H.; Famini, G. R.; Doherty, R. M.; Kamlet, M. J. *J. Pharm. Sci.* **1985**, *74*, 807.

(6) Kamlet, M. J.; Taft, R. W., unpublished information.

0022-3263/86/1951-2130$01.50/0