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On the Transition State For "Clayzic"-Catalyzed Friedel-Crafts Reactions Upon Anisole

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Key Words: Unimodal kinetics - activation parameters - chemisorption - Lewis acid

Abstract: *The activation parameters point to a strongly organized transition state on the catalyst surface, with partial breaking of the carbon-leaving group bond in the BnCl or in the Ac_2O reagent.*

Based upon our report on the Friedel-Crafts prowess of ion-exchanged montmorillonites,[1] an heterogeneous catalyst has been devised for Friedel-Crafts reactions, zinc chloride impregnated on an industrial montmorillonite clay, K10.[2] Nicknamed "clayzic", it is efficient in alkylation[1,3] or acylation[4]. Whereas zinc chloride is a weak Lewis acid[5] and correspondingly a relatively poor Friedel-Crafts catalyst[6], impregnation on a clay turns the kitten into a tiger! Side-product inhibition was exploited to observe the catalytic sites present in "clayzic": in all likelihood, the most active sites are located on the edges of the clay platelets[7]. Furthermore, when Friedel-Crafts reactions catalyzed by "clayzic" are run in competitions between two substrates, synergistic accelerations[8], reactivity upheavals[9], counterintuitive selectivities[10], and even competitive inhibition[11] occur. In the latter case, we[12] and others[13] have shown the explanation to be selective chemisorption as the rate-determining step in a Langmuir-Hinshelwood mechanism. Besides such enzyme-like aspects, "clayzic" as a catalyst presents the advantage of lesser (by up to three orders of magnitude) amounts than demanded of the standard Lewis acids used in Friedel-Crafts processes[1]. This has been put to industrial and commercial use[14].

Returning to competitive inhibition, observed when alkylating toluene in mixtures of benzyl chloride and benzyl alcohol, it is due to the alcoholic oxygen binding strongly onto the zinc catalytic centers[12]. In order to test the conjecture that chemisorption could be rate-determining for the reactions of anisole, as it is with alcohols[12], we launched the present kinetic study. It doubles up as a comparative analysis of the kinetic behaviors of anisole in benzylation and acylation.

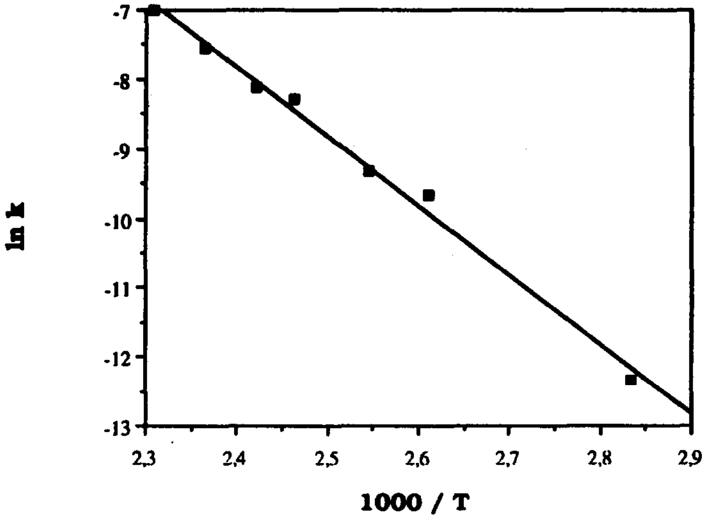


Figure 1: Arrhenius plot for acylation of anisole (ρ = 0.995 for 7 points).

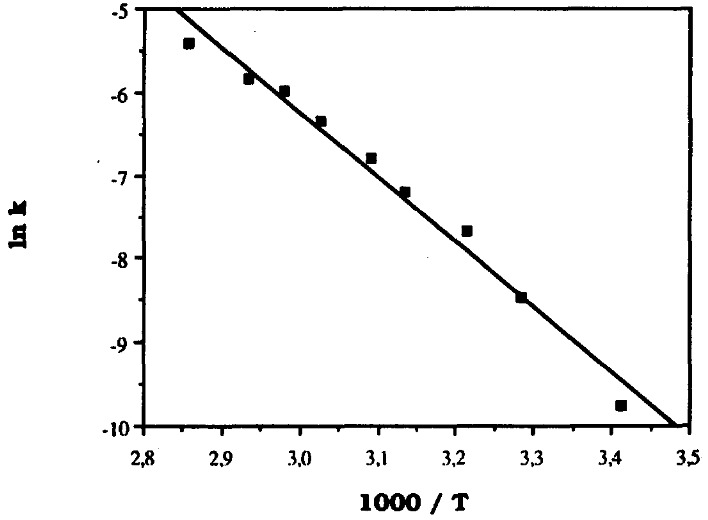


Figure 2: Arrhenius plot [15] for benzylation of anisole (ρ = 0.996 for 9 points)

Conditions are stirring (400 rpm) a mixture of 100 mmol anisole, 10 mmol BnCl or Ac_2O and 0.25 g of "clayzic" 4/1 [4, 8-12] at various temperatures, in the whole accessible temperature range: for benzylation 20-80 ± 0.5 °C; for acylation 80-160 ± 0.5 °C. Stirring is maintained and samples are taken repeatedly during the whole reaction, and analyzed by GC. Conversion of the benzyl chloride (acetic anhydride) reactant defines the rate constant: it is monitored by GC with n-tetradecane (n-hexadecane) as internal standard. Under these conditions, it is checked that pseudo first-order kinetics are obeyed. Product concentrations x (A_0 denotes the initial concentration) and pseudo first-order parameters $\ln |A_0 - x| = - kt + \ln A_0$ values plotted against reaction time (s) were prepared and inspected for linearity. The slopes were determined along with the linear correlation coefficients. The rate constants (maximum errors < 5 %) plotted against reciprocal absolute temperature are displayed in Figs. 1-2.

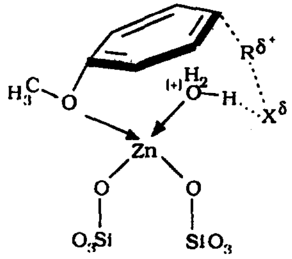
The corresponding Arrhenius and Eyring parameters are listed in Table 1:

Table 1. Kinetic parameters (standard deviation)

	ln A	E_a, $kJ.mol^{-1}$	$\Delta H^‡$, $kJ.mol^{-1}$	$\Delta S^‡$, $J.mol^{-1}.K^{-1}$
acylation	16.3^5 (0.9)	83.0 (3.1)	80.5 (3.5)	- 118 (11)
benzylation	17.3 (0.8)	65.0 (2.0)	62.3 (3.2)	- 113 (9)

Anisole chemisorption is not rate-determining: if it were, the activation parameters would be identical in both reactions, contrary to observation (Table). Rather, the transition state must involve a measure of stretching of the carbon-chlorine bond in the BnCl, and of the carbon-oxygen bond in the Ac_2O reagents. The difference in the enthalpies of activation, 18 kJ. mol^{-1} indeed reflects the greater stability of the benzyl as compared to the acetyl cation.[17] The strongly negative values for the entropy of activation point to highly ordered transition states. Two, non mutually exclusive pictures that come to mind are (i) attack by the Ac_2O or BnCl reagent via its Lewis basic center, oxygen or chlorine, on the zinc Lewis acid already coordinated, in a pre-equilibrium, to anisole; (ii) Brønsted acid catalysis of leaving group exit by the superacidic clay surface, with the acidity of the remaining water molecules enhanced through coordination to zinc (II) [18]. While their absolute values are larger, the $\Delta H^‡$ and $\Delta S^‡$ from the Table are highly reminiscent of those measured in benzylation of anisole with titanium tetrachloride as the catalyst, viz. 52 kJ. mol^{-1} and - 74 J. mol^{-1}. K^{-1} [19]: the "clayzic" catalyst acts like a normal Lewis acid catalyst, except for the much lower amounts required.

In schematic form, the transition states evoked by these and previous[1-12] results on "clayzic" are the following:



Acknowledgements

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2. Manufactured by Süd-Chemie, München, Germany, it is sold by various suppliers of chemicals (Aldrich and Janssen, for instance). Following a treatment, that we have reason to believe is acid washing and calcination, K10 contains amorphous together with well-crystallized domains. Pinnavaia has shown it to be a mesoporous solid, with pore dimensions in the 30-50Å range: Butruille, J.-R.; Pinnavaia, T.J. *Catal. Today*, **1992**, *14*, 141-154.
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14. under the name Envirocats, by Contract Chemicals, Penrhyn Road, Knowsley Industrial Park, Prescot, Merseyside, L34 9HY, England.
15. We did not deem it advisable, on account of the limited experimental accuracy, to treat it as deviating from a straight line. Yet visual inspection suggests a sigmoidal variation. If chemisorption by the mesoporous catalyst is the rate-determining step, one may expect the corresponding isotherm a = f(T) to have a sigmoidal shape [16]; which would carry over, through the Langmuir-Hinshelwood equation, of the form: rate = ka[BnCl]/(1 + a [BnCl]) [12] into the Arrhenius plot.
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