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Explanation of a Paradoxical Selectivity in Friedel-Crafts Alkylation Under Heterogeneous Catalysis.

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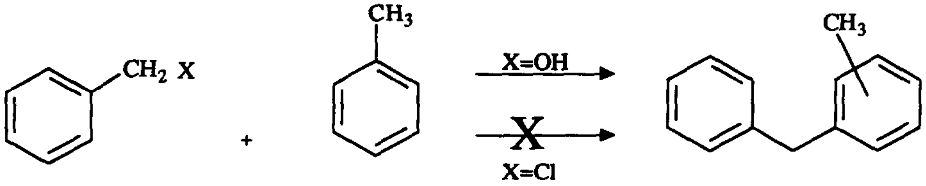
Key Words : one-pot reactions – micro-reactors – Langmuir-Hinshelwood model – preferential adsorption.

Abstract *: The earlier reported selectivity favoring benzyl alcohol over benzyl chloride in the alkylation of toluene with "clayzic" as the catalyst, with conversion of the alcohol taking precedence over that of the chloride, arises from competitive inhibition. Alcohols in general poison the active centers of the catalyst. With i-amyl alcohol as a probe, the alcohol is adsorbed preferentially to benzyl chloride by a factor 600, in the Langmuir-Hinshelwood model.*

In the presence of the K10 montmorillonite clay impregnated with zinc chloride[1-2] ("clayzic", for short), addition of benzene improved significantly competitive Friedel-Crafts alkylation of a co-reactant such as toluene, mesitylene, or p-xylene[3]. Besides such synergism, the presence of a co-reactant can also invert the relative reactivities: whereas toluene was more reactive than mesitylene in separate alkylations, a one-pot reaction favored mesitylene[4]. Likewise, mesitylene was benzoylated faster/slower than anisole in separate/joint reactions[5]. A fascinating fact from this earlier set of observations was that, whereas benzyl chloride (BnCl) is normally more reactive than benzyl alcohol (BnOH) toward aromatic hydrocarbons, at 20°C alkylation of toluene is totally inhibited in the presence of an equimolar mixture of the two benzylating agents and of "clayzic". At 80°C, all the alcohol molecules were first consumed. Then, and only then, 45 mn after the onset of the reaction, the chloride molecules started their reaction[6]. We focus here exclusively on this last finding of substrate selectivity allied with such sequential behavior. We provide experimental evidence for competitive inhibition of BnCl by BnOH.



The first part of the proof is the general finding that alcohols poison the "clayzic" catalyst. With a BnCl concentration in toluene, serving as its own solvent, of about 1 M, 50 mM concentrations of a variety of alcohols (methanol – t-butanol – 2-pentanol – cyclohexanol – cinnamyl alcohol – citronellol) are sufficient to block conversion of benzyl chloride into the tolylphenylmethane product, at 80°C [7].

In order to both quantify the inhibition and ascertain which mechanistic step is involved, we needed alcohols less reactive than BnOH, that would inhibit the catalyst without reacting with the toluene substrate. Methanol was too volatile for this purpose, and we elected i-amyl alcohol (2-pentanol; AmOH) whose boiling point (119-120°C) is compatible with the 80°C reaction temperature.

Conditions are one-shot addition of the "clayzic" catalyst (250 mg) to a mixture, pre-heated to the reaction temperature (80°C), of benzyl chloride (10 mmol), 2-pentanol (0.1-1 mmol), and of toluene in excess (100 mmol). Conversion of benzyl chloride is monitored by GC, and a n-hexadecane standard is used to determine the yields of monobenzylated products. Depending upon the concentrations of the alcoholic poison, the reaction times vary from about 30 mn to 8 h.

The two mechanistic possibilities that were considered were (i) a simple pseudo first-order process: $[\mathrm{BnCl}] = [\mathrm{BnCl}]_0 \exp(-kt)$;
and (ii) combination of a pseudo first-order reaction with an adsorption pre-equilibrium on the catalyst (Taylor postulate)[8].

The latter corresponds to a reaction rate of the form:

$$\frac{k\, a\, [\mathrm{BnCl}]}{1 + a\, [\mathrm{BnCl}]} \qquad (1)$$

If indeed the Taylor postulate is applicable, the inhibitor blocks a fraction of the active centers on the catalyst: to be more specific, the concentration of BnCl at the catalytic surface is reduced by the presence of the AmOH co-adsorbate[9]. Such a model, as originally proposed by Langmuir [10-11-12] results in a reaction rate of the modified form:

$$\frac{1 + a\, [\mathrm{BnCl}]}{1 + a\, [\mathrm{BnCl}] + b\, [\mathrm{AmOH}]} \qquad (2)$$

The parameters a and b measure the adsorption constants of the BnCl reagent and of the AmOH inhibitor, respectively. The experimental kinetic curves are better reproduced by equation 2. The results compared with (equation 2) and without (equation 1) the inhibitor are analysed[13] for the b/a ratio (Table):

Table 1. Ratio of the adsorption constants of i-amyl alcohol (b) and of benzyl chloride (a) at various inhibitor concentrations.

[AmOH], mM	b/a
22	541
38	611
48	561
63	600

The self-consistency of these results[14] supports the validity of the Langmuir-Hinshelwood model[15] (equation (2)): BnCl and AmOH are co-adsorbed on "clayzic", and the former much less than the latter, by a factor 580 ± 30. This conclusion ties in nicely with the well-known strength of zinc-oxygen bonds and thus corroborates the notion of zinc active centers on the "clayzic" catalyst.

It was not a self-evident conclusion from the start. "Clayzic" catalyzes separate alkylation reactions by BnCl and BnOH. That the alcohol also poisons the very catalyst that converts it into alkylated product is a somewhat paradoxical but uncontrovertible finding. Such behavior differs from that of other poisoned catalysts. The Lindlar catalyst, also very familiar to organic chemists, and consisting of palladium supported on calcium carbonate poisoned by lead and by quinoline, works by facilitated product desorption with minimal influence on the adsorption of the reactants[16]. Here, the "clayzic" catalyst when poisoned with 2-pentanol works by blocking adsorption of the benzyl chloride reactant.

In our earlier papers on molecular recognition by montmorillonite-based catalysts[3-6], we were careful to refrain from speculation on the origin of the reported effects. We contented ourselves with the phenomenological comment that "microscopic robots consisting of smectite clay-based catalysts effect the batch processing of chemicals"[6]. In particular, we were very careful not to attribute the results to a version of shape selectivity consisting of a sieving by the lamellar support.

The significance of these findings is that substrate selectivity, of such an exquisite fine tuning that it discriminates between benzene and toluene, or between toluene and mesitylene, may be due simply to chemisorption onto an inorganic solid, in the absence of shape selectivity due to diffusion within a microporous solid. The practical importance is obvious. The implications for the origins of life, of molecular recognition on specks of dirt, contaminated with the ubiquitous zinc cation[17], and those for biomimetic[17] enzyme models based on clays are also worthy of note.

To sum up the explanation of the inhibition of BnCl by BnOH we return to the descriptive mode: like 2-pentanol, the BnOH molecules adsorb onto the catalytic surface preferentially to their BnCl co-reactant. They tie-up the Zn(II) catalytic sites. Thus, the BnOH molecules are activated by the Lewis acidic centers while blocking access to their BnCl rivals[24].

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References

1 - Laszlo, P.; Mathy, A. *Helv. Chim Acta* **1987**, *70*, 557-586.
2 - Clark, J. A.; Kybett, A. P.; Barlow, D. J.; Landon, P. *J. Chem. Soc. Chem. Comm.* **1989**, 1353-1354.
3 - Cornélis, A.; Dony, C.; Laszlo, P.; Nsunda, K. M. *Tetrahedron Lett.* **1991**, *32*, 1423-1424.
4 - Cornélis, A.; Dony, C.; Laszlo, P.; Nsunda, K. M. *Tetrahedron Lett.* **1991**, *32*, 2901-2902.
5 - Laszlo, P.; Montaufier, M.-T. *Tetrahedron Lett.* **1991**, *32*, 1561-1564.
6 - Cornélis, A.; Dony, C.; Laszlo, P.; Nsunda, K. M. *Tetrahedron Lett.* **1991**, *32*, 2903-2904.
7 - We did also test ethers as poisons: not quite as effective as alcohols. Methyl t-butyl ether (MTBE) is thus less of a poison than t-butanol by a factor 3.5.
8 - J. E. Germain "Catalyse hétérogène," Dunod: Paris, 1959, p 68;
I. M. Campbell "Catalysis at Surfaces," Chapman and Hall: London, 1988, pp 37-43.
9 - Ashmore, P. G. "Catalysis and Inhibition of Chemical Reactions," Butterworths: London, 1963.
10 - Langmuir, I.*J. Am. Chem. Soc.*, **1915**, *38*, 2221.
11 - Langmuir, I. *J. Am. Chem. Soc.* **1918**, *40*, 1361.
12 - Langmuir, I. *Trans. Faraday Soc.* **1922**, *17*, 621.
13- The value of k^{-1} obtained in the absence of the inhibitor through equation 1 is assumed to hold as well in the presence of the inhibitor (equation 2). In this manner, the integrated rate laws for the four entries (or eight runs) of Table 1 are (in the same sequence as in Table 1, first without the inhibitor and second with the inhibitor) and with c denoting [BnCl]:

$t = -0.172\,(c-10) - 4.973\,\ln(c/10)$; $t = -0.172\,(c-10) - 26.711\,\ln(c/10)$
$t = -0.103\,(c-10) - 1.087\,\ln(c/10)$; $t = -0.103\,(c-10) - 26.546\,\ln(c/10)$
$t = -0.195\,(c-10) - 2.146\,\ln(c/10)$; $t = -0.195\,(c-10) - 57.997\,\ln(c/10)$
$t = -0.336\,(c-10) - 1.614\,\ln(c/10)$; $t = -0.336\,(c-10) - 136.579\,\ln(c/10)$

14 - Another internal check is provided by the self-consistency, within a fair approximation, of the values of the rate constant $k = 0.6 \pm 0.3\ \mathrm{mn}^{-1}$ obtained from equation (2) alone.
15 - Adamson, A. W. "Physical Chemistry of Surfaces," 5th ed., Wiley: New York, 1990, pp 717-721.
16 - Bond, G. C. "Heterogeneous Catalysis. Principles and Applications," Clarendon Press: Oxford, 1987, pp 53-54.
17 - Among metallic ions, Zn(II) ions stand out for the highly stable complexes they form, with very high rates of formation and very small dissociation rates[18]. Zinc is stable only in the +2 state and cannot perform redox reactions. Its Lewis superacidity specializes it conversely as a general catalyst for biological acid-catalyzed reactions[19]. It owes it to one of the highest values for the Z_{eff}/r ratio[20]. This gives zinc (II) a high polarizing power. As a d^{10} metal, this ability at polarization is isotropic, which favors flexible coordination of ligands[21]. Indeed many carbonyl-polarizing enzymes (carboxypeptidase[22,23]for instance) use Zn(II) for this purpose.
18 - Eigen, M.; Hammes, G.G. *Adv. Enzymol.* **1963**, *25*, 1-38.
19 - Williams, R.J.P. *Coord. Chem. Rev.* **1990**, *.100*, 573-610.
20 - Ochiai, E-I. *J. Chem. Ed.* **1988**, *65*, 943-946.
21 - Drenth, J. *Recl. Trav. Chim. Pays-Bas* **1980**, *99*, 185-190.
22 - Lipscomb, W.N. *Tetrahedron*, **1974**, *30*, 1725-1732.
23 - Lipscomb, W.N. *Proc. Natl. Acad. Sci. USA* **1980**, *77*, 3875-3878.
24 - Thus one may seek in the differential adsorption of, say anisole and mesitylene, the explanation for the other, less dramatic reactivity inversions that we had reported earlier.

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