

Spectroscopic Evidence for the Involvement of a Radical Intermediate in the Friedel-Crafts Benzylation Using Ion-Exchanged K10 Catalysts

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Abstract

For Friedel-Crafts alkylation of aromatic hydrocarbons an ionic reaction path is considered as classical reaction mechanism. The alkylation with benzyl chloride in the presence of ion-exchanged K10 montmorillonite catalysts containing multivalent, reducible cations had an outstanding activity, therefore a radical initial step as a supplement to the ionic mechanism was proposed earlier. We made ESR investigations to clarify the existence and the nature of the suggested radical species. The ESR experiments verified that the reaction involves a radical step.

Keywords

Friedel-Crafts alkylation, benzylation, radical step, ESR spectroscopy

1 Introduction

Friedel-Crafts reaction is one of the most important reactions of organic chemistry and chemical industry [1, 2]. It serves to functionalize aromatic compounds, providing useful intermediates of different classes of materials, such as pharmaceuticals, dyes, surfactants, and agrochemicals. Nowadays instead of the traditional Lewis acids (AlCl_3 , FeCl_3 , ZnCl_2) heterogeneous acid catalysts are used more and more in these reactions [3], in order to facilitate the separation of the catalyst as well as the work-up of the reaction mixture, to avoid the corrosion and the formation of large amount of waste water, and yielding environmentally more benign processes. A great number of acidic heterogeneous catalysts are suitable for Friedel-Crafts reactions (see e.g. the list in [4]), the use of the clay-based ones is very advantageous because of the good activity, low price and simple preparation process.

We investigated in detail the alkylation of benzene and toluene with benzyl alcohol as well as benzyl chloride, using ion-exchanged K10 clays as catalysts [5]. The kinetic evaluation of the reactions showed that using benzyl alcohol as alkylating agent the initial reaction rate was proportional to the Brønsted acidity of the catalysts, but

in the case of benzyl chloride there was no correlation between the reaction rate and neither the Brønsted, nor the Lewis acidity. At the same time in this latter reaction the catalysts containing multivalent, reducible cations (Fe^{3+} , Cu^{2+} , Sn^{2+}) had an outstanding activity. This observation suggested that the reaction involves an oxido-reductive process, therefore we have proposed a radical initial step as a supplement to the classical ionic mechanism.

Exactly the same radical part-process was proposed later by Choudary et al. [6], without mentioning at all our precedent proposition.

The possibility of a radical step has arisen also on the basis of other reactions carried out in the presence of clay-based catalysts, in liquid phase, where the presence of radicals or radical cations was proved: nitration of aromatic hydrocarbons or phenols [7-10], Diels-Alder reaction between methyl acrylate and cyclopentadiene [11].

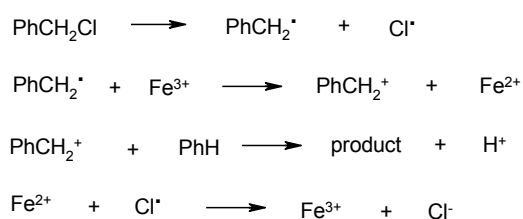
Three probable mechanistic interpretations can be found in the literature for benzylation of aromatic hydrocarbons with benzyl chloride on solid acid based supported metal catalysts, without any direct (preparative or spectroscopic) experimental verification: a simple radical

step [12–17] – see Scheme 1; the presence of a benzyl chloride radical cation [4, 18–25] – see Scheme 2; or the presence of a benzyl radical cation [26–28] as intermediate – see Scheme 3. In some cases the same authors have different suggestions for similar catalytic systems.

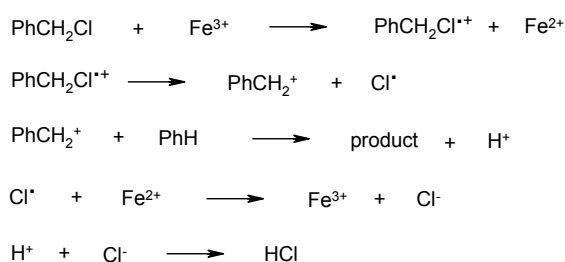
For an experimental support of our proposition and for the sake of orientation between the three suggested mechanism variants we have investigated by ESR spectroscopy whether a radical is formed in the reaction, and in a positive case what is its structure.

2 Results and discussion

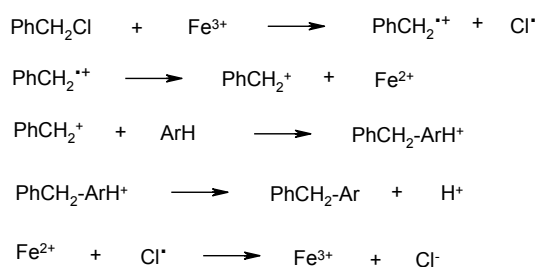
Mixing benzyl chloride, toluene and Fe^{3+} -K10 clay in an ESR tube a sharp singlet appeared even at room temperature at $g = 2.0037$ with 20 G linewidth (Fig. 1). This is characteristic to a carbon-type radical. Since the signal



Scheme 1 Proposed reaction mechanism for Friedel-Crafts benzylation of benzene with benzyl chloride over iron-containing mesoporous TUD-1 catalyst [12].



Scheme 2 Proposed reaction mechanism for Friedel-Crafts benzylation of benzene with benzyl chloride over iron-modified ZSM-5 zeolites [18].



Scheme 3 Proposed reaction mechanism for Friedel-Crafts benzylation of benzene with benzyl chloride over iron mesoporous silicas [28].

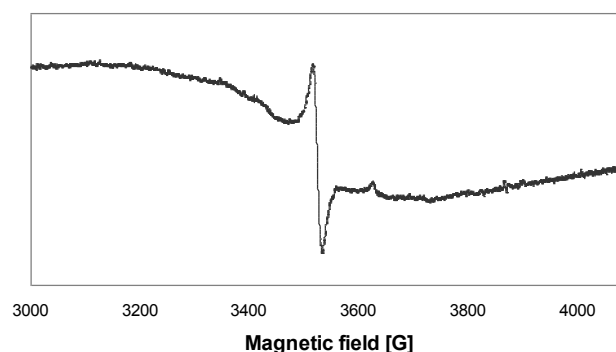


Fig. 1 Signal obtained in the reaction of benzyl chloride with toluene in the presence of Fe^{3+} -K10.

was obtained also when toluene was omitted from the reaction mixture, the radical can be unambiguously originated from benzyl chloride. Nevertheless, a benzyl-type radical should show multiplicity. The large linewidth and the lack of multiplicity can be explained with either the solid surface of the catalyst or the oxygen adsorbed on the bulk solid phase which can hinder the splitting of the signal. The intensive evolution of HCl which resulted the foaming of the mixture in the sample tube might also disturbed the observation of a clear liquid phase. The evolution of the signal was quite fast, and the signal reached a maximum after about a half an hour (Fig. 2).

The formation of the radical was continuous, after a fast rise its concentration reached a maximum value (Fig. 3, left). Simultaneously, the concentration of Fe^{3+} in the solution reached a maximum (Fig. 3, right).

Next we examined the other metal-modified K10 catalysts, the reaction of which showed outstanding reactivity in our former benzylation experiments [5]. Thus, when Sn^{2+} -K10 was used instead of Fe^{3+} -K10, a similar signal having the same g value and linewidth was detected (Fig. 4).

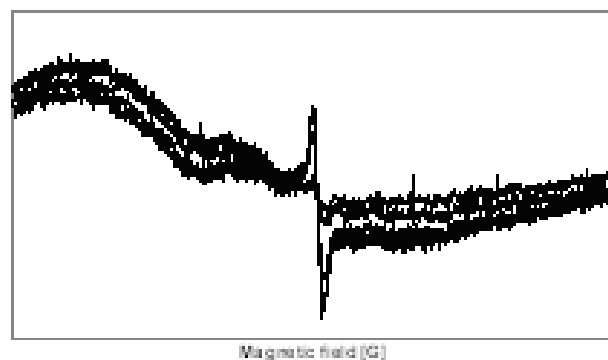


Fig. 2 Evolution of the signal detected in the reaction of benzyl chloride with toluene in the presence of Fe^{3+} -K10 in the range of 0 – 1508 sec.

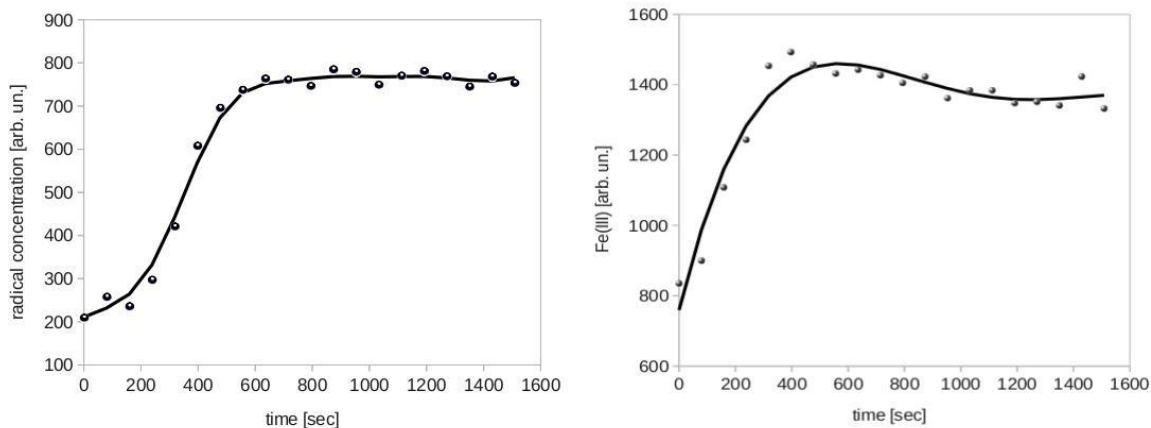


Fig. 3 Evolution of the concentration of the radical (left) and the Fe^{3+} ion (right) in the sample.

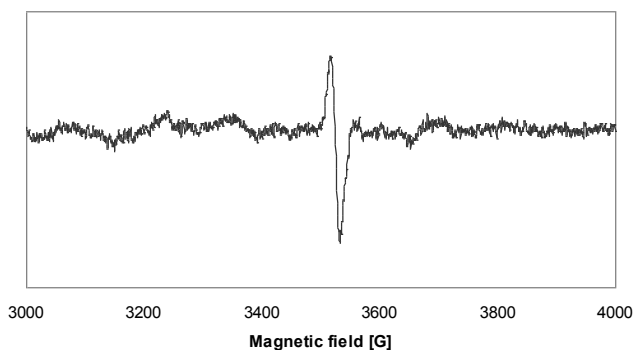
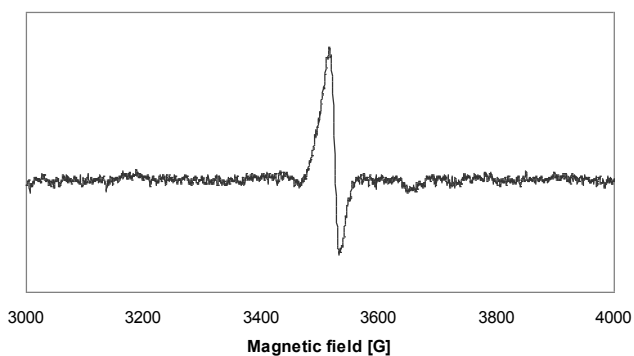


Fig. 4 Signal obtained in the reaction of benzyl chloride with toluene in the presence of Sn^{2+} -K10.

The other catalysts, which showed enhanced reactivity in the Friedel-Crafts alkylation of benzene or toluene with benzyl chloride, were the copper- and manganese-modified K10 clays. These metals have a strong disturbing effect on the ESR-measurements. However, we could detect the same signal when benzyl chloride was treated with Cu^{2+} -K10 and Mn^{2+} -K10 (Fig. 5).



These experiments support our initial hypothesis [5] on a radical step in clay-catalysed Friedel-Crafts benzylation with benzyl chloride. The signals obtained, however, could not help in the exact determination of the nature of the radical. Thus DFT calculations were made [29] to decide between a benzyl radical or a benzyl radical cation (see Schemes 1 and 3). The spectra were calculated with 1 G linewidth (this gives better approximation of the shape of the signal) and to minimal energy (this estimates better the linewidth). The results are shown on Fig. 6.

The linewidth of the calculated signal is more comparable with the measured linewidth in the case of the benzyl radical. For the benzyl radical cation the difference between the calculated and measured linewidth is unreally big. The lack of the splitting in the case of benzyl radical can be explained with the disturbing effects during the measurement indicated above (foaming, the solid surface and the oxygen adsorbed on this surface). Thus we can suppose that from the previous proposition described for this type of Friedel-Crafts alkylation the mechanism depicted in Scheme 1 may describe the run of the reaction.

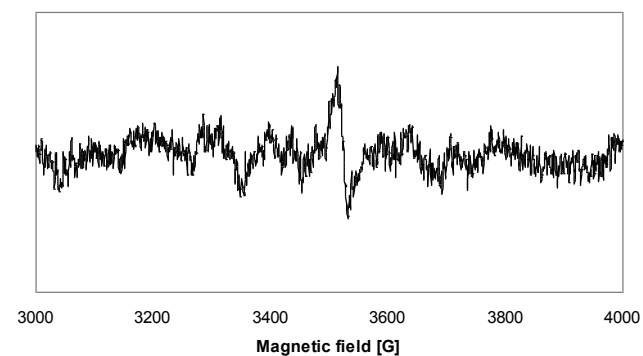


Fig. 5 Signal obtained in the reaction of benzyl chloride with toluene in the presence of Cu^{2+} -K10 (left) and Mn^{2+} -K10 (right).

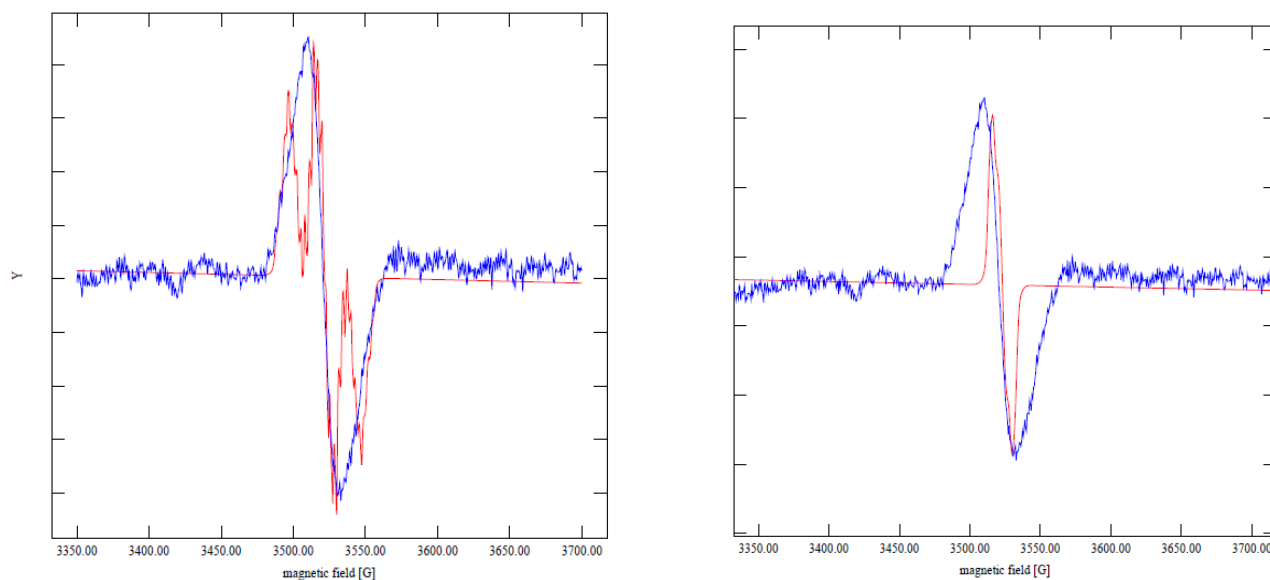


Fig. 6 Comparison of the measured signal and the signal calculated for benzyl radical (left) and benzyl radical cation (right) (blue: measured signal, red: calculated signal).

3 Experimental

3.1 Generalities

Benzyl chloride and toluene were purchased from Merck Ltd. Hungary. K10 montmorillonite was the product of Süd-Chemie (Germany).

^1H NMR spectrum was recorded on a Bruker Avance-300 spectrometer. The sample was dissolved in CDCl_3 . Chemical shifts are given on a δ scale, $\delta(\text{TMS}) = 0$ ppm.

ESR spectra were recorded on a Bruker EleXsys 500 instrument. 100K modulation frequency, 10 G modulation and 10 mW microwave power were used.

TLC-s were developed on Merck Kieselgel 60 F_{254} plates with hexane/acetone (4:1) eluent.

3.2 Preparation of the catalysts

K10 clay was exchanged as described earlier [5] with Cu^{2+} , Fe^{3+} , Mn^{2+} , and Sn^{2+} . Thus the clay was gradually added to a stirred aqueous solution of the chloride of the cation at room temperature for 24 h. After the exchange the suspensions were filtered and washed with deionized water to eliminate the physisorbed salts. The resulting solids were dried on a thin layer at 373 K and ground. The thus obtained K10 catalysts are designated as Me^{n+} -K10.

3.3 Reaction of benzyl chloride with toluene

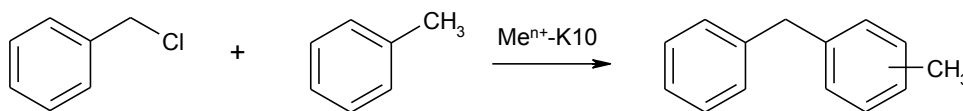
The mixture of 0.79 g (0.72 cm^3 , 6.25 mmol) benzyl chloride and 0.1 g Me^{n+} -K10 in 10 cm^3 toluene was stirred at $80 \text{ }^\circ\text{C}$ for 3.5 h (complete consumption of benzyl chloride, checked by TLC). Then the solid was filtered off, the filtrate was evaporated. The residue was subjected to a ^1H NMR analysis. The spectral data showed the presence of 1-benzyl-2-methylbenzene and 1-benzyl-4-methylbenzene in a 1:1 ratio. δ : 2.21(s, 3H), 2.28(s, 3H), 3.91(s, 2H), 3.95(s, 2H), 7.04-7.25(m, 18H).

3.4 ESR experiments

Benzyl chloride, toluene and Fe^{3+} -K10 montmorillonite was placed in an ESR tube. Vigorous evolution of HCl was observed after a few minutes even at room temperature. The experiments were repeated with Sn^{2+} -, Cu^{2+} -, and Mn^{2+} -modified K10, too. In every case a well-developed ESR signal was detected.

4 Conclusions

ESR experiments verified that the Friedel-Crafts reaction of toluene with benzyl chloride in the presence of K10 clay modified with Fe^{3+} , Cu^{2+} , Mn^{2+} or Sn^{2+} ions involves a



Scheme 4 Reaction of benzyl chloride with toluene in the presence of modified K10 clay

radical step. Based on the ESR spectra and theoretical calculations, this radical may be a benzyl radical.

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† In memoriam Sándor Békássy



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