ON THE MECHANISM OF THE CLAY CATALYZED REACTION OF BENZYLAMINE

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<u>Summary</u> The mechanism of the aluminum exchanged Montmorillonite catalyzed reaction of benzylamine was studied with deuterium labelled benzylamine. From the analysis of the product dibenzylamine and the recovered benzylamine extensive hydrogen exchange is observed. An SN₂ process is thus unlikely and a process involving an imine is suggested.

We wish to report the results of experiments that provide insights into the mechanism of the clay catalyzed reaction of primary amines to give secondary amines and the elimination of ammonia.¹⁻² A proposed mechanism involves a proton-catalyzed substitution reaction similar to the related reactions of alcohols and thiols.³

However oxidation reduction mechanisms should be considered and are possibly more likely. Laszlo has shown that radical cations (from oxidation) are probable intermediates in many clay catalyzed reactions.⁴ Indeed tertiary amines are employed as scavengers for radical cations. Moreover there are some observations that are incompatible with a displacement reaction. While aniline does not give the diamine reaction the presence of aniline totally inhibits reaction of normally reactive amines.³ Such an inhibiting effect is compatible with the importance of oxidation reduction processes whereas no obvious explanation derives from a displacement reaction.

Such oxidation schemes applied to the amine reactions would likely involve imines, and in fact, in the production of secondary amines from primary amines over nickel and palladium surfaces, the imine and Schiff bases have been identified as key intermediates.⁵ An imine intermediate is suggested in the nickel boride reduction of nitrocyclohexane to account for the formation of dicyclohexylamine.⁶ Moreover imines are observed in the clay catalyzed amine reaction.² An alternate mechanism which can account for these observations involves the steps depicted below.

 $\begin{array}{ccc} \text{RCH}_2\text{NH}_2 & \xrightarrow{\text{OXID}} & \text{RCH}=\text{NH} \\ \text{RCH}=\text{NH} + & \text{RCH}_2\text{NH}_2 & \longrightarrow & \text{RCH}=\text{NCH}_2\text{R} + & \text{NH}_3 \\ \text{RCH}= & \text{NCH}_2\text{R} + & \text{R-CH}_2 - & \text{NH}_2 & \longrightarrow & \text{RCH}_2\text{NHCH}_2\text{R} + & \text{RCH}=\text{NH} \end{array}$

Thus two mechanisms are candidates for the reaction of primary amines to give secondary amines: a substitution reaction and an oxidation sequence involving imines. Our experimental approach seeks to differentiate between these by labelling experiments. We reacted benzylamine- α , α -d₂ in a clay-catalyzed reaction and monitored for loss of deuterium in the product dibenzyl amine and starting material.

The compound benzylamine- α , α -d₂ was prepared in 73% yield from the reaction of benzonitrile and lithium aluminum deuteride (98%d). Analysis by proton and carbon-13 NMR spectroscopy revealed this material to be 97% deuterated, with both the d1 and d0 benzylamine present. (Table 1)

The deuterated benzylamine (5.0g 0.47 mol) was heated with 1.0 g of Al exchanged Montmorillonite (SWy-1) at 180° for 60 hours in a glass apparatus with a reflux condenser. The reaction mixture was extracted with methylene chloride and filtered. The methylene chloride was removed (rotovap) to give a quantitative recovery of material.

Gas chromatographic analysis of the material showed 72% benzylamine and 28% dibenzylamine and no other compounds present in amounts greater than 0.5%. The proton NMR spectra of the mixture showed that the alpha position (of both the starting material and product) contained .37 hydrogens. Thus 30% of the deuteriums had exchanged for hydrogen during the reaction.

The analysis is further supported and expanded by the results of the ¹³C NMR spectra. First in the carbon spectra the alpha carbons for benzyl amine and dibenzyl amine are clearly separated and independent analysis is possible. Second, the d-2, d-1 and d-0 materials are clearly distinguished by both chemical shift and coupling differences, and it is possible to obtain the extent of isotopic substitution in both the starting material and product. Table I records the proton and ¹³C NMR results for the initial deuterated amine, the products of reaction and a control reaction.

The results in Table I indicate where 28% of the benzyl amine is converted to dibenzylamine 30% of the alpha deuteriums of the benzyl amine and the product dibenzylamine have been exchanged. In a control reaction where there is no conversion to debenzylamine 5% of the deuteriums have exchanged for hydrogen. The exchange of alpha deuteriums in benzylamine is catalyzed by the clay catalyst and involves protons available from either the amine protons or the extensive water and/or hydroxyl protons present on the catalyst.

The results of the exchange reaction demand lability of the alpha hydrogens and formation of an intermediate in a reversible process. Moreover the exchange of the benzyl deuteriums for protons must occur with a source of hydrogens for example the NH or catalyst OH protons. A most reasonable intermediate for this reversible exchange is the imine. That this exchange reaction occurs on the same time scale as the dimerization reaction infers that this same imine intermediate is responsible for both the exchange and the reaction.

The remarkable formation of secondary amines from primary amines with clays has precedent. In 1972 Richey and Erickson discovered a base catalyzed formation of secondary amines from primary amines.⁷ The mechanism they propose involves imines. Interestingly there are many important parallels in the results and conclusions between the base catalyzed and acid clay catalyzed reactions. Foremost among these is the enhanced selectivity for a mixed product when benzyl amine and an aliphatic amine are reacted together. Richey and Erickson comment that this " ...indicates the different roles played by the two amine molecules...". This selectivity for the base catalyzed reaction.

We propose that the considerable selectivity in the clay catalyzed reaction is similarly accounted for by the same relative imine stabilities, that is, benzyl imine is far more stable than hexyl or cyclohexyl imine. Selectivity between amines is then determined by the thermodynamic stability of the relevant imines which is independent of mechanism for imine generation. Therefore the product determining steps of both the acid and base catalyzed proceses are the same.

Purnell and Ballantyne considered an imine intermediate for the clay catalyzed reaction but rejected this mechanism for several reasons.² First, they argue that the selectivity in cross reactions can be accounted for by basicity (pK) differences and therefore reactivity for an SN₂ process of the two amines. Second, since the imine scheme requires a final hydrogenation they note the absence of a hydrogenation catalyst.

An explanation for the large selectivities in an SN₂ process based on the small basicity difference (1.3pK units) of the amines is unlikely for the following reasons. The effectiveness of a nucleophile in an SN₂ process is determined by oxidation potential as well as basicity, and in this regard, benzyl amine might prove to be a more potent nucleophile than cyclohexane amine. Additionally, the 1.3 pK difference between benzyl amine and cyclohexylamine at 25°C would be greatly moderated at 200°C. Finally, only some fraction of the basicity differences between the two bases would contribute directly to the rate differences. Therefore only small if any reactivity differences would be expected for an SN₂ process based on these considerations.

The final step in the proposed scheme involves conversion of an imine to an amine. In the clay catalyzed (or base reaction) the hydride transfer to imine is somewhat problematical. In hydrogenation reactions this conversion of the Schiff base is catalyzed by the metal catalyst. For the clay and base catalyzed reactions there is no traditional transition metal present for the final hydrogenation. However there is an alternate possibility involving the aluminum exchanged clay. The source of hydrogen in these reactions is depicted below in a sequence similar to the hydrogen transfer in the Meerwein-Pondorff-Verley-Oppenauer reaction. A similar scheme is proposed for the base catalyzed reaction.⁷ Moreover the aluminum ion is involved in catalysis of carbon nitrogen double bonds in the aluminum isopropoxide conversion of oximes to carbonyls.⁸



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Table 1. Deuterium Content at Alpha Position^a

<u>Compound</u>	<u>Benzylamine</u>			<u>Dibenzylamine</u>		
	d2	d 1	d0	d2	d1	d0
Starting Material	95.5	3.0	1.5			
Control ^b	90.1	8.4	1.5			
Product Mixture	67. 8	27.0	5.2	66.0	33.5	2.4

- a Determined by ¹H and ¹³C NMR Spectroscopy.
- ^b The amine was heated with the unexchanged clay Montmorillonite (SWY-1) under identical conditions as the reaction with the AI exchanged clay. The unexchanged clay is inactive for the amine dimerization.²

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