

## **LiAl(OPr<sup>i</sup>)<sub>4</sub> as a Model Compound for the Conjugate Base of the Zeolite Catalyst H-ZSM-5 and its Reaction with Various Methylating Agents**

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LiAl(OPr<sup>i</sup>)<sub>4</sub> has been shown to demethylate a range of methylating agents including the trimethyloxonium ion; no products due to ylide formation were observed suggesting that a surface-bound trimethyloxonium ion ylide is an unlikely reaction intermediate in the methanol conversion process.

In the conversion of methanol to hydrocarbons using H-ZSM-5 zeolite<sup>1</sup> and other catalysts,<sup>2</sup> the mechanism of formation of the first carbon-carbon bond is a matter of considerable controversy. The available experimental evidence strongly indicates the involvement of an oxonium ylide intermediate<sup>3,4</sup> which Olah<sup>2</sup> has suggested undergoes intermolecular methylation after binding to a bifunctional acid-base catalyst. With regard to the formation of the oxonium ylide by deprotonation, recent work<sup>5</sup> has shown that while deprotonation of the oxonium ion is possible with very strong non-nucleophilic

bases, *e.g.* 2,2,6,6-tetramethylpiperidyl-lithium or NaH,<sup>2</sup> demethylation is observed with strong bases like Bu<sup>s</sup>Li. Therefore, since the conjugate base of H-ZSM-5 is weak, the question arises as to the nature of the ylide formation step. As a model compound for the conjugate base of H-ZSM-5 we have taken LiAl(OPr<sup>i</sup>)<sub>4</sub>, in which a negatively charged aluminium is tetrahedrally co-ordinated by 4 oxygen units as in the active site, and in which silyloxy groups are replaced by isopropoxy groups.<sup>6</sup> In this study we compare the relative nucleophilicity and basicity of the tetraisopropoxide ion

**Table 1.** Composition of reaction distillates.

Expt.	Nucleophilic source	Methylating agent	Relative % molar compositions <sup>b</sup>			% Conversion <sup>c</sup> into Pr <sup>i</sup> OMe
			Pr <sup>i</sup> OMe	Pr <sup>i</sup> Cl	Pr <sup>i</sup> OH	
1	Al(OPr <sup>i</sup> ) <sub>3</sub>	Me <sub>3</sub> O <sup>+</sup> SbCl <sub>6</sub> <sup>-</sup>	12	31	57	2.5
2	LiAl(OPr <sup>i</sup> ) <sub>4</sub>	"	27	31	42	7
3	Pr <sup>i</sup> OH	"	19	32	49	8
4	LiAl(OPr <sup>i</sup> ) <sub>4</sub>	MeSO <sub>3</sub> F	47	0	53	27
5	Al(OPr <sup>i</sup> ) <sub>3</sub>	"	38	0	62	10
6 <sup>a</sup>	Pr <sup>i</sup> OH	"	0	0	100	
7	LiAl(OPr <sup>i</sup> ) <sub>4</sub>	Me <sub>2</sub> SO <sub>4</sub>	8	0	92	5
8	Pr <sup>i</sup> OH	"	0	0	100	
9	LiAl(OPr <sup>i</sup> ) <sub>4</sub>	Me <sub>3</sub> S <sup>+</sup> I <sup>-</sup>	0	0	100	

<sup>a</sup> Pr<sup>i</sup>OH (16 mg, 0.27 mmol) was treated with MeSO<sub>3</sub>F (115 mg, 1 mmol) in C<sub>6</sub>D<sub>6</sub> (4 ml). <sup>b</sup> Relative % compositions were calculated from the n.m.r. integrations. <sup>c</sup> Based on 1 mmol production of ether to be 100%.

towards a series of methylating agents including the trimethyloxonium ion.

Al(OPr<sup>i</sup>)<sub>3</sub><sup>7</sup> (1 mmol) and LiAl(OPr<sup>i</sup>)<sub>4</sub><sup>8</sup> (1 mmol) were treated separately in C<sub>6</sub>D<sub>6</sub> (4 ml) with Me<sub>3</sub>O<sup>+</sup>SbCl<sub>6</sub><sup>-</sup> (1 mmol) at room temperature. In each run the reaction mixture was heated to reflux (80 °C) and the solvent and volatile products were then distilled into a trap at -60 °C using a dry nitrogen carrier gas. The total reaction time was of the order of 20 min and on average a 3 ml distillate was collected. Product compositions were analysed by g.c. and n.m.r. spectroscopy and the relative % molar compositions and conversions are listed in Table 1.

Since the reactions were conducted under extremely dry conditions as evidenced by only a relatively small quantity of MeOH among the products, the generation of Pr<sup>i</sup>OH must have been due to a breakdown of the aluminium species. This possibility is further supported by the observation that longer reaction times with LiAl(OPr<sup>i</sup>)<sub>4</sub> (e.g. reflux 30 min prior to distillation) produced considerably more Pr<sup>i</sup>OH with the MeOH content staying virtually constant. Moreover blank experiments with either aluminium compound in C<sub>6</sub>D<sub>6</sub>, CCl<sub>4</sub>, or CDCl<sub>3</sub> produced protonated Pr<sup>i</sup>OH indicating that the alcohol does not arise by deprotonation of solvent. Me<sub>2</sub>O and MeCl, although detected when a short-fraction distillate was taken, were not detected to any great extent in the recorded experiment on account of their volatility. Conversions as seen in Table 1 were under 10%.

The Pr<sup>i</sup>Cl could have been generated from either Pr<sup>i</sup>OH or Pr<sup>i</sup>OMe *via* chloride attack on a Lewis acid-bound species or on an isopropyl carbocation. Indeed Pr<sup>i</sup>OMe did give some Pr<sup>i</sup>Cl when treated with LiSbCl<sub>6</sub> in a blank experiment. However the important feature of the results of experiments 1-3 is that regardless of whether the ratio of ether to alcohol or ether and chloride to alcohol is taken, the reaction with the much less soluble tetraisopropoxide shows a relatively greater ratio in favour of ether than that using the tri-isopropoxide or the blank using Pr<sup>i</sup>OH. Indeed it may be argued that since the blank reaction involved a relatively large quantity of Pr<sup>i</sup>OH being added all at once to the alkylating agent, the more representative blank run is the reaction with the tri-isopropoxide in which the amount of ether as expected is much lower.

The results indicate that LiAl(OPr<sup>i</sup>)<sub>4</sub> quite readily provides an isopropoxide unit (only 1 equiv. assumed likely) for demethylation whereas the neutral Al(OPr<sup>i</sup>)<sub>3</sub> does not to any great extent. Moreover, no trace of any MeOEt<sup>5</sup> was detected, implying that the tetraisopropoxide ion is much more nucleophilic than basic.

In order to provide further evidence for its nucleophilicity, LiAl(OPr<sup>i</sup>)<sub>4</sub> was treated separately with MeSO<sub>3</sub>F ('magic methyl') and Me<sub>2</sub>SO<sub>4</sub> on a 1 mmol scale (1:1 stoichiometry) in C<sub>6</sub>D<sub>6</sub> (4 ml). Owing to the stability of the methylating agents, it was possible to give the reactions a longer contact time (reflux 30 min), and MeSO<sub>3</sub>F (27% conversion) was shown to be a superior methylating agent than Me<sub>2</sub>SO<sub>4</sub> (5% conversion), consistent with their methylating power for hard nucleophiles.<sup>7</sup> A blank run showed Pr<sup>i</sup>OH to be insufficiently nucleophilic to demethylate either of the methylating agents while Al(OPr<sup>i</sup>)<sub>3</sub> did give some Pr<sup>i</sup>OMe although in lower yield (10% conversion). Finally the reaction between Me<sub>3</sub>SI and LiAl(OPr<sup>i</sup>)<sub>4</sub> was examined. In this experiment neither MeSEt nor Pr<sup>i</sup>OMe were detected showing that the tetraisopropoxide ion is not sufficiently basic to generate the sulphur ylide nor sufficiently nucleophilic to demethylate the relatively poorly electrophilic sulphonium ion.

While Olah has indicated<sup>2</sup> that surface-bound Me<sub>2</sub>O-catalyst donor-acceptor complexes can give rise to surface-bound oxonium ylides in his bifunctional acid-base system, this type of species is impossible with the conjugate base of H-ZSM-5. Moreover, we consider that these results shed doubt on the conjugate base deprotonating a trimethyloxonium ion to give an ylide as proposed by van den Berg,<sup>3</sup> owing to its poor basicity. Instead we suggest that the conjugate base might well be methylated by a suitable species such as the oxonium ion, protonated MeOH, or Me<sub>2</sub>O, which then undergoes further reaction *via* an active site-incorporated ylide.

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## References

- C. D. Chang and A. J. Silvestri, *J. Catal.*, 1977, **47**, 249.
- G. A. Olah, H. Doggweiler, J. D. Felbeg, S. Frohlich, M. J. Grdina, R. Karpeles, T. Kevmi, S. Laba, W. M. Ip, K. Lamertsmas, G. Salem, and D. C. Tabar, *J. Am. Chem. Soc.*, 1984, **106**, 2143.
- J. P. van den Berg, J. P. Wolthuizen, and J. H. C. van Hoof, Proceedings of the 5th Conference on Zeolites, Naples, Italy, 1980, p. 649.
- G. A. Olah, *Pure Appl. Chem.*, 1981, **53**, 201.
- P. Rimmelin, H. Taghari, and J. Sommer, *J. Chem. Soc., Chem. Commun.*, 1984, 1210.
- D. C. Bradley, R. C. Mehrota, and D. P. Gaur, 'Metal Alkoxides,' Academic Press, London, 1978.
- H. C. Brown and R. F. McFarlin, *J. Am. Chem. Soc.*, 1958, **80**, 5372. Commercially available from Merck-Schuchardt.
- D. N. Kevill and G. M. C. Lin., *Tetrahedron Lett.*, 1978, 949.