Kinetics of methylamine conversion on a Pd catalyst in the presence of H₂

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The kinetics of disproportionation of methylamine to dimethylamine and ammonia in the presence of hydrogen have been investigated over a silica-supported palladium catalyst. At a fixed partial pressure of methylamine, the reaction rate generally increases with decreasing hydrogen partial pressure, approaching a limiting or maximum value at sufficiently low pressures of hydrogen. The existence of a maximum is supported by the observation that the presence of some hydrogen appears to be necessary for the reaction to proceed at a conveniently measurable rate. At a fixed hydrogen partial pressure, the reaction rate increases with increasing methylamine partial pressure. When the methylamine partial pressure is sufficiently low or the hydrogen partial pressure is sufficiently high, the reaction order with respect to methylamine can be somewhat higher than one. At such conditions, a mechanism involving a bimolecular reaction between two partially dehydrogenated methylamine molecules on the surface appears to make a significant contribution to the overall catalytic reaction.

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1. Introduction

When mixtures of methylamine and hydrogen are contacted with a variety of metal catalysts, two principal reactions are observed, hydrogenolysis and disproportionation[1–3]. Hydrogenolysis produces methane and ammonia as products:

\[ \text{CH}_3\text{NH}_2 + \text{H}_2 \rightarrow \text{CH}_4 + \text{NH}_3 \] (1)

The products of the disproportionation reaction are dimethylamine and ammonia:

\[ 2\text{CH}_3\text{NH}_2 \rightarrow (\text{CH}_3)_2\text{NH} + \text{NH}_3 \] (2)

The relative amounts of hydrogenolysis and disproportionation differ markedly from one metal to another [3]. Thus, hydrogenolysis is the only significant reaction observed on rhodium [3]. In marked contrast, on palladium, the extent of hydroge-
Hydrogenolysis is small compared to disproportionation. Moreover, trimethylamine is formed to some extent on palladium [1–3].

Reaction (1) is similar to the hydrogenolysis reaction of ethane, in which a molecule of ethane reacts with a molecule of hydrogen to form two molecules of methane [4,5]. However, a disproportionation reaction of ethane yielding propane and methane as products, analogous to reaction (2) of methylamine, does not occur beyond a trace amount on palladium or on any of the metals, although it is thermodynamically feasible. It is intriguing that the catalytic chemistry of the carbon–nitrogen bond differs from that of the carbon–carbon bond in this respect.

Two different views of the mechanism of disproportionation of methylamine to dimethylamine and ammonia have been suggested in the literature [1,2]. In both, the initial chemisorption of methylamine yields a partially dehydrogenated methylamine molecule on the surface. Without a specification of the hydrogen content of this species, it is convenient to represent the species by the structural unit \([C-N]\) reflecting the carbon–nitrogen skeleton. Scission of the carbon–nitrogen bond then yields carbon and nitrogen fragments of unspecified hydrogen content which are designated, for simplicity, as \([C]\) and \([N]\),

\[
[C-N] \rightarrow [C] + [N].
\]  

(3)

For the remainder of this Introduction, we use brackets \([\ ]\) to indicate surface species of unspecified hydrogen content. The mechanism of disproportionation proposed by Kemball and Moss [1] included the step

\[
[C-N] + [C] \rightarrow [C-N-C]
\]  

(4)

to produce a surface species with the carbon–nitrogen skeleton characteristic of dimethylamine. In an alternative scheme to account for such a species, Anderson and Clark [2] proposed the bimolecular step

\[
[C-N] + [C-N] \rightarrow [C-N-C-N]
\]  

(5)

followed by a step involving scission of the appropriate carbon–nitrogen bond,

\[
[C-N-C-N] \rightarrow [C-N-C] + [N].
\]  

(6)

In either of the proposed mechanisms, hydrogenation of the species \([C-N-C]\) and \([N]\) with accompanying desorption yields the reaction products dimethylamine and ammonia. The proposal of Anderson and Clark was based in part on isotopic tracer studies employing methylamine, methane, or ammonia labeled with \(^{13}\)C or \(^{15}\)N.

In particular, these workers did not observe a direct exchange reaction between \(^{13}\)CH\(_3\)NH\(_2\) and CH\(_3\)^{15}NH\(_2\) yielding \(^{13}\)CH\(_3\)^{15}NH\(_2\) as a primary reaction product. From this result, they concluded that the scission of the C–N bond in a partially dehydrogenated methylamine molecule on the surface is irreversible. Since the chemisorbed fragments of the scission do not exhibit the reverse reaction to form a C–N bond, Anderson and Clark expressed the opinion that C–N bond formation by the reaction represented by eq. (4) is also unlikely. However, this view is debata-