Kinetics of methylamine conversion on a Pd catalyst in the presence of H_2

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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.

Keywords: methylamine disproportionation: (1) kinetics of; (2) catalysis of, by palladium; (3) mechanism of; (4) effect of hydrogen pressure on

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:

$$CH_3NH_2 + H_2 \rightarrow CH_4 + NH_3 . \qquad (1)$$

The products of the disproportionation reaction are dimethylamine and ammonia:

$$2CH_3NH_2 \rightarrow (CH_3)_2NH + NH_3 . \qquad (2)$$

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 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],

$$[\mathrm{C{-}N}] \rightarrow [\mathrm{C}] + [\mathrm{N}]. \qquad (3)$$

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

$$[\mathrm{C{-}N}] + [\mathrm{C}] \rightarrow [\mathrm{C{-}N{-}C}] \qquad (4)$$

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

$$[\mathrm{C{-}N}] + [\mathrm{C{-}N}] \rightarrow [\mathrm{C{-}N{-}C{-}N}] \qquad (5)$$

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

$$[\mathrm{C{-}N{-}C{-}N}] \rightarrow [\mathrm{C{-}N{-}C}] + [\mathrm{N}]. \qquad (6)$$

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 debatable. Consequently, these workers cited as additional evidence for their mechanistic proposal some very limited kinetic data indicating a second-order dependence of the disproportionation rate on methylamine pressure.

In view of the two different proposals regarding the reaction mechanism, we have conducted a more extensive investigation of the kinetics of methylamine disproportionation to dimethylamine and ammonia over a palladium catalyst. Reaction rates were determined over a wide range of methylamine and hydrogen partial pressures at several different temperatures. The results are discussed in terms of the two mechanistic proposals.

2. Experimental

Reaction rates were measured at a total pressure of 1 atm in a flow system which has been described previously [3]. The reactor was a vertical stainless-steel tube, approximately 30 cm long and 1.0 cm in diameter, surrounded by a small furnace. The catalyst was used in the form of 40/60 mesh granules diluted with ground Vycor beads of the same particle size. A typical charge consisted of 0.2 g of catalyst diluted with 0.5 g of the ground Vycor. The diluted catalyst occupied a space approximately 1.3 cm in length and was located halfway between the inlet and outlet of the reactor. It was supported on an 80 mesh stainless-steel screen held in place by a 3 mm axial thermowell which extended upward through the screen into the catalyst bed. The tip of the thermowell, which contained an iron–constantan thermocouple, was located at the center of the bed. Reaction in the presence of the Vycor alone, or in admixture with the silica carrier used in the Pd/SiO_2 catalyst, was negligible throughout the range of temperatures employed in this work.

In a typical run, methylamine and hydrogen were diluted with helium and passed downflow through the catalyst bed. The total flow rate of the gas was 1 ℓ/min. The flow rates of the methylamine, hydrogen, and helium were metered separately prior to mixing of the gases in a section of stainless-steel tubing leading to the reactor. The desired partial pressures of the reactants were obtained by controlling the flow rates appropriately. The gas mixture was passed over the catalyst for a period of 5 min, at which time the reactor exit gas was sampled for chromatographic analysis. The flow of methylamine was then discontinued, after which a flow of hydrogen and helium was maintained over the catalyst for a period of 15 min prior to another run.

Reaction products containing carbon were analyzed with a Hewlett-Packard model 5880 gas chromatograph employing two glass columns 3 m in length (2 mm i.d.) connected in series. A flame ionization detector was used. The columns, which were obtained from Supelco, Inc., Bellefonte, PA, contained 60/80 mesh Carbopack B impregnated with 4% Carbowax 20M plus 0.8% KOH. They were operated at 50°C with a flow rate of 33 $cm^3\ min^{-1}$ of helium carrier gas. This analytical procedure does not provide information on the amount of ammonia in the reactor effluent. Consequently, an infrared analyzer (Beckmann Instruments model No. 8650-9900-5000) was used for the determination of ammonia yields. Since the amount of ammonia determined in this way agreed very well with the amount expected from the analysis for the other products over a wide range of reaction conditions, many of the experimental runs did not include analysis for ammonia.

The Pd/SiO_2 catalyst used in the kinetic studies contained 1 wt% Pd and had a metal dispersion (ratio of surface Pd atoms to total Pd atoms) of 0.1 as determined by carbon monoxide chemisorption [3]. It was prepared by impregnation of a form of silica known as Cab-O-Sil HS5 (300 m^2/g surface area) with an aqueous solution of palladium nitrate. After the impregnation step, the material was dried overnight in air at 380 K, and then contacted with flowing hydrogen for 2 h at 725 K to reduce the palladium. The resulting palladium catalyst was then purged with helium and cooled to room temperature, after which it was passivated by controlled exposure to air and stored in a closed container until needed. After a sample of catalyst was charged to the reactor, it was again contacted with hydrogen at 725 K to ensure that the palladium was fully reduced.

The methylamine used in the experiments was obtained from the Matheson Company. It contained a small amount of dimethylamine as an impurity, along with trace quantities of ammonia and trimethylamine. In the determination of rates of formation of dimethylamine, a correction was made for the amount introduced with the reactants. The hydrogen used in the experiments had a nominal purity of 99.999%.

3. Results

While the disproportionation reaction of methylamine as represented by eq. (2) does not show participation of hydrogen, the presence of hydrogen in the reactant gases nevertheless appears to be necessary for the reaction to proceed, at least at a conveniently measurable rate. Thus, when a freshly reduced sample of the palladium catalyst was purged with helium at the reduction temperature and subsequently cooled in helium to 498 K, passage of a mixture of methylamine and helium (3 mol% CH_3NH_2) over the catalyst did not produce a detectable amount of reaction. However, when hydrogen was present in the mixture, the disproportionation reaction was readily observed.

The selectivity of conversion of methylamine to carbon-containing products (dimethylamine, trimethylamine, and methane) at low conversions (1–5%) is shown in table 1 for various sets of reaction conditions. The only other product is ammonia. Dimethylamine is the predominant carbon-containing product. Trimethylamine and methane are formed to a much smaller extent. In our studies of the kinetics of conversion of methylamine to dimethylamine, reaction rates were determined at conversion levels in the approximate range of 0.2–10%. At these low conversions, the yield of dimethylamine was always one to two orders of magnitude higher than that of methane.

Table 1
Selectivity of conversion of methylamine to carbon-containing products [a]

Temperature (K)	Partial pressures (atm)		Selectivity (%) [b]		
	MA	H_2	DMA	TMA	CH_4
458	0.01	0.20	80	19	1
458	0.01	0.90	91	8	1
458	0.10	0.20	88	12	
458	0.10	0.90	87	13	
498	0.01	0.20	92	4	4
498	0.01	0.90	96		4
498	0.10	0.20	96	2	2
498	0.10	0.90	96	2	2

[a] At low conversions, in the range of 1–5%. Methylamine, dimethylamine, and trimethylamine are designated, respectively, by the symbols MA, DMA, and TMA.

[b] Percentage of converted methylamine appearing as DMA, TMA, and CH_4.

Maintenance of catalytic activity did not present a problem in the kinetic studies, as was established by repeated determinations of the reaction rate at a standard set of conditions during a series of measurements at varying conditions. The molar ratio of hydrogen to methylamine was generally higher than 1, and about 90% of the data were obtained at ratios varying from 2 to 90. This factor is undoubtedly important in the maintenance of catalytic activity, since very low H_2/CH_3NH_2 ratios might be expected to enhance the formation of surface residues which contain fewer hydrogen atoms than the surface species involved in the reaction. The more highly hydrogen-deficient species are likely to be irreversibly adsorbed and thereby to serve as catalyst poisons. This phenomenon is well known in catalytic reforming and related processes [6,7].

The results of the kinetic studies are presented in fig. 1, in which the natural logarithm (molecules per second per palladium atom in the catalyst) is shown as a function of the natural logarithm of the hydrogen partial pressure (expressed in atmospheres). The data are divided into three different fields, corresponding to three different temperatures. In each field, methylamine partial pressure is the parameter distinguishing the different data sets. It increases in the direction from the lowest to the uppermost set of data points. The curves in fig. 1 were obtained by fitting the data to a rate equation to be considered subsequently.

The reaction rate at a fixed methylamine pressure generally increases with decreasing hydrogen partial pressure, approaching a limiting or maximum value at the lowest hydrogen partial pressures for which data are shown in fig. 1. The existence of a maximum is supported by the observation that the reaction does not occur to a measurable extent in the complete absence of hydrogen. To obtain a clearer definition of the maximum, it would be necessary to extend the range of data of fig. 1 to still lower hydrogen partial pressures. Unfortunately, accurate rate

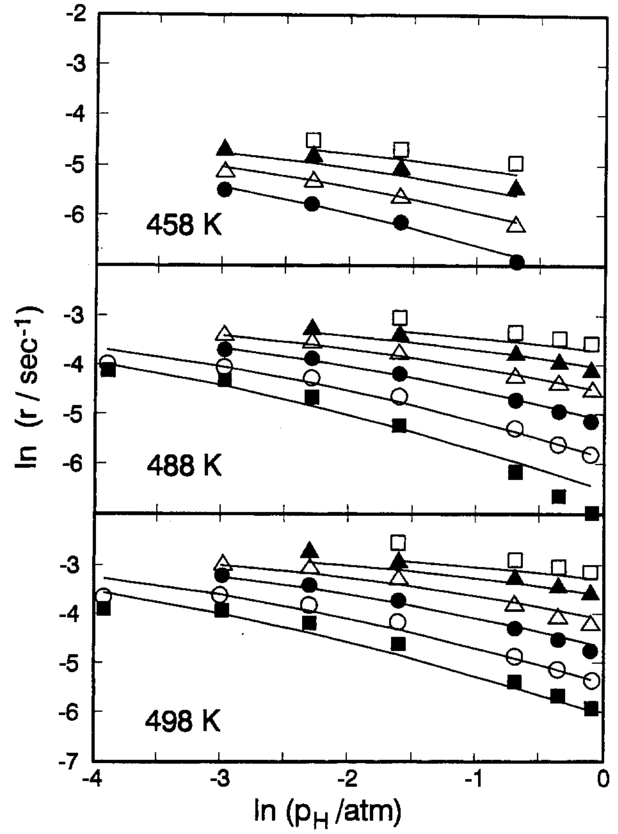


Fig. 1. Kinetics of disproportionation of methylamine to dimethylamine and ammonia over a Pd/SiO_2 catalyst. The catalyst contained 1 wt% Pd and had a metal dispersion (ratio of surface Pd atoms to total Pd atoms) of 0.1. Data on the natural logarithm of the reaction rate r (in molecules of dimethylamine formed per second per Pd atom in the catalyst) are shown as a function of the natural logarithm of the hydrogen partial pressure p_H (in atm) at a series of methylamine partial pressures: (■) 0.010 atm; (○) 0.015 atm; (●) 0.025 atm; (△) 0.040 atm; (▲) 0.065 atm; (□) 0.10 atm. The curves in the figure were obtained by fitting the rate data to eq. (7) in the text.

data could not be obtained at such conditions because of experimental limitations with the existing apparatus.

At a fixed hydrogen partial pressure, the reaction rate increases as the partial pressure of methylamine increases. It is particularly interesting that the reaction order with respect to methylamine over part of the range of data is higher than one. Under certain conditions a reaction order of two is approached. This happens when the methylamine partial pressure is sufficiently low or the hydrogen partial pressure is sufficiently high.

The data in fig. 1 are described reasonably well by an empirical rate expression of the form

$$r = k\{bA/(1+bA)\}^2, \tag{7}$$

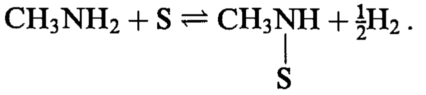
where k and b are temperature dependent parameters and the quantity A is defined as the ratio of the methylamine partial pressure p_{M} to the square root of the hydrogen partial pressure p_{H},

$$A = p_{\mathrm{M}}/p_{\mathrm{H}}^{1/2}. \tag{8}$$

The curves in fig. 1 show the quality of fit of eq. (7) to the data. Values of the experimental rate constant k and the parameter b at three different temperatures are given in table 2. Since the dispersion of the palladium in the catalyst is 0.1, rates per surface palladium atom are higher by a factor of 10 than rates obtained either from fig. 1 or from eq. (7) using the values of the kinetic parameters in table 2. The temperature dependence of k corresponds to an activation energy of 19.3 kcal/mol. The significance of the parameter b and of conclusions based on its temperature dependence are considered in the subsequent discussion.

4. Discussion

Available evidence indicates that the chemisorption of methylamine on palladium and platinum occurs predominantly at the nitrogen atom rather than the carbon atom. First, Kemball showed that deuterium undergoes exchange with the hydrogen atoms in ammonia much more readily than with the hydrogen atoms in methane on both of these metals [8,9]. Second, with methylamine itself, Kemball and Wolf found that these metals selectively catalyzed the exchange of deuterium with the hydrogen atoms bonded to nitrogen in the molecule [10]. Moreover, the exchange occurred at temperatures substantially lower than those required for catalyzing the disproportionation reaction of methylamine. Thus, it seems reasonable to assume that the initial step in the disproportionation reaction is the formation of a partially dehydrogenated methylamine intermediate CH_3NH bonded to a site S on the metal surface,



$$CH_3NH_2 + S \rightleftharpoons \underset{\substack{|\\ S}}{CH_3NH} + \tfrac{1}{2}H_2. \tag{9}$$

Table 2
Kinetic parameters for the conversion of methylamine to dimethylamine on a Pd catalyst [a]

Temperature (K)	k (s^{-1})	b ($atm^{-1/2}$)
458	0.015	17.5
488	0.054	19.7
498	0.081	20.4

[a] The parameters k and b are defined by eq. (7) in the text.

With regard to subsequent steps, the proposal of Anderson and Clark [2] of a bimolecular reaction between two partially dehydrogenated methylamine molecules on the surface provides a reasonable way of accounting for the observation that the reaction rate varies with methylamine partial pressure raised to a power somewhat greater than one over part of the range of conditions covered by the investigation. We conclude, therefore, that such a mechanism makes a significant contribution to the overall reaction.

In proceeding with a kinetic analysis based on the Anderson and Clark type of mechanism, we assume first that the step represented by eq. (9) is equilibrated. If the partially dehydrogenated intermediate CH_3NH is assumed to be the only chemisorbed species of significance, a rate expression of the form of eq. (7) can be shown to apply if a bimolecular reaction between two chemisorbed CH_3NH radicals is important in the overall transformation occurring on the palladium.

The parameter b in eq. (7) would then be an equilibrium constant for the initial step represented by eq. (9). Since table 2 shows that b increases slightly with increasing temperature, the initial step would therefore be endothermic (by an amount of 1.7 kcal/mol). The corresponding entropy change calculated from the data in table 2 would then be +9.5 e.u. (e.u. = entropy unit = cal mol^{-1} deg^{-1}). Since the standard molar entropy of hydrogen in the gas phase at 498 K is approximately 35 e.u. [11], the entropy of the dehydrogenated methylamine intermediate of eq. (9) would be lower than that of the methylamine in the gas phase by only 8 e.u. With a value of approximately 65 e.u. for the standard molar entropy of methylamine at 498 K [12], the entropy of the intermediate would be 57 e.u. The intermediate would be highly mobile on the surface. However, this conclusion is inconsistent with the assumption of immobile adsorption underlying the representation of an adsorption equilibrium by a classical Langmuir isotherm [13–15]. Consequently, the identification of the parameter b in eq. (7) as an adsorption equilibrium constant for simple Langmuir adsorption lacks rigor.

Thus, a Langmuir form of rate expression as embodied in eq. (7) fits the data for the catalytic conversion of methylamine to dimethylamine reasonably well over a broad range of conditions, but careful scrutiny of the parameter b reveals the limitation of the analysis. Attempts to modify the analysis via hypothesis of a more highly dehydrogenated surface intermediate (i.e., a species such as CH_3N or $CH_2{=}NH$ bonded to a site S) did not resolve this difficulty, and the modified rate expression gave a poorer fit to the data. The ability of a Langmuir form of rate equation to fit kinetic data, despite the fact that a simple adsorption equilibrium described by a Langmuir adsorption isotherm may not be applicable in a particular situation, has been recognized previously [16–18]. In some situations, an adsorption equilibrium may not be involved at all. Thus, a Langmuir form of rate equation is applicable to a reaction sequence consisting of a series of irreversible steps, but the ratio of the rate constants for two of the steps replaces an adsorption equilibrium constant in the equation [16–18]. In the present investigation, however, we were not able to make a satisfactory analysis of the kinetic data by considering such a sequence.

The failure of a simple kinetic analysis based on the Anderson and Clark type of mechanism to provide a description of the data in terms of parameters which are totally free from objection on physical grounds may simply be an indication of the complexity of the system. Kinetic effects due to a non-uniform catalytic surface could be a contributing factor. Alternatively, the possibility of two different reaction pathways contributing to the overall reaction may be another factor. Thus, our kinetic data do not rule out the possibility that a pathway of the type suggested by Anderson and Clark [2], as represented by eqs. (5) and (6) in the Introduction of this paper, is accompanied by a second pathway of the type proposed by Kemball and Moss [1] embodied in eqs. (3) and (4).

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