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Kinetics of hydrogenolysis of methylamine on a rhodium catalyst

G. Meitzner, W.J. Mykytka and J.H. Sinfelt

Corporate Research, Exxon Research and Engineering Company,
Annandale, NJ 08801, USA

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The kinetics of hydrogenolysis of methylamine to methane and ammonia were investigated over a catalyst consisting of small clusters of rhodium dispersed on silica. Data obtained in the temperature range 353–408 K exhibit a characteristic pattern in which the rate passes through a maximum as the hydrogen partial pressure is increased by two orders of magnitude from 0.01 to 1.0 atm. At a given temperature, the position of the maximum shifts slightly in the direction of higher hydrogen partial pressure when the methylamine partial pressure increases by one to two orders of magnitude. Of particular interest is the finding that the rate increases with decreasing methylamine partial pressure over a broad range of hydrogen partial pressures covered in the investigation. As the hydrogen pressure increases, the inverse dependence of the rate on methylamine pressure becomes less pronounced and eventually disappears at a sufficiently high hydrogen pressure. At hydrogen partial pressures somewhat higher than those at which the rate maxima are observed, there is some indication that the inverse dependence changes to a positive dependence, especially at the lowest temperatures investigated. It seems likely that the rate limiting step of the reaction changes when the hydrogen pressure varies over a wide range. At the highest hydrogen pressures studied, it is suggested that the limiting step is one in which the scission of the carbon–nitrogen bond occurs in a hydrogen deficient surface intermediate formed in the chemisorption of methylamine, with no direct participation of hydrogen as a reactant in the step. On the other hand, at the lowest hydrogen pressures investigated, it is proposed that the rate is limited by a step in which chemisorbed hydrogen does participate directly as a reactant.

Keywords: methylamine hydrogenolysis: (i) kinetics of; (ii) catalysis of, by rhodium; (iii) mechanism of; (iv) effect of hydrogen pressure on; (v) effect of methylamine pressure on

1. Introduction

When methylamine is contacted with various metal catalysts in the presence of hydrogen, several reactions occur, of which hydrogenolysis and disproportionation are the most common [1–3]. The former yields methane and ammonia as products, while the latter produces dimethylamine and ammonia:

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

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

On palladium the disproportionation reaction predominates [1–3]. However, on rhodium, the only reaction observed is hydrogenolysis [3].

In a study of the catalytic activities of the 4d metals Ru through Pd and of the 5d metals Re through Au for the hydrogenolysis of methylamine, rhodium was found to be the most active [3]. In view of the high catalytic activity of rhodium for this reaction, and the absence of competing reactions of methylamine on this metal, we decided to make an extensive investigation of the kinetics of methylamine hydrogenolysis on a rhodium catalyst. Rate data were obtained over a wide range of hydrogen and methylamine partial pressures at a series of different temperatures in the range of 353–408 K. The results of the investigation are presented herein.

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 Rh/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.

Methylamine, methane, and other compounds containing carbon in the reactor effluent were analyzed with a Hewlett-Packard model 5880 gas chromatograph employing a glass column 6 m in length (2 mm i.d.). A flame ionization detector was used. The column, which was obtained from Supelco, Inc., Bellefonte, PA, contained 60/80 mesh Carbopack B impregnated with 4% Carbowax 20M plus 0.8% KOH. It was operated at 80°C with a flow rate of 33 cm^3 min^{-1} of nitrogen carrier gas. An infrared analyzer (Beckmann Instruments model No. 8650-9900-5000) was used for the determination of ammonia in the exit gas from the reactor.

The Rh/SiO_2 catalyst used in the kinetic studies contained 1 wt% Rh and had a metal dispersion (ratio of surface Rh atoms to total Rh atoms) of 1.0 as determined by hydrogen 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 rhodium trichloride. 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 rhodium. The resulting rhodium 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 the sample of catalyst was charged to the reactor, it was again contacted with hydrogen at 725 K to ensure that the rhodium 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. The hydrogen used in the experiments had a nominal purity of 99.999%.

3. Results

Hydrogenolysis was the only significant reaction observed when mixtures of methylamine and hydrogen were passed over the rhodium catalyst in the present investigation. Although the exit gas from the reactor in a given run was analyzed for both the methane and ammonia formed in the reaction, the infrared analysis for the latter was generally less reliable than the chromatographic analysis for the former. This was most evident for reactor exit gases with very low concentrations of ammonia. Therefore, rates of hydrogenolysis were determined from the amounts of methane found in the exit gases from the reactor.

Maintenance of catalytic activity did not present a problem in the kinetic studies. The possibility of a significant decline in catalytic activity might be expected to increase as the ratio of hydrogen to methylamine in the inlet stream to the reactor decreases. However, even at the lowest ratios employed in the five-minute reaction periods, the fifteen-minute treatment of the catalyst with the hydrogen–helium mixture between reaction periods was routinely successful in maintaining catalytic activity at a constant level. There was no evidence for irreversible incorporation of nitrogen or carbon in the catalyst.

Rates of formation r of methane, in molecules per second per surface rhodium atom, are given in fig. 1 in the form of curves showing the dependence on hydrogen partial pressure p_H at a constant methylamine partial pressure p_M, for a series of different values of the latter. A different symbol is used for the data points at each

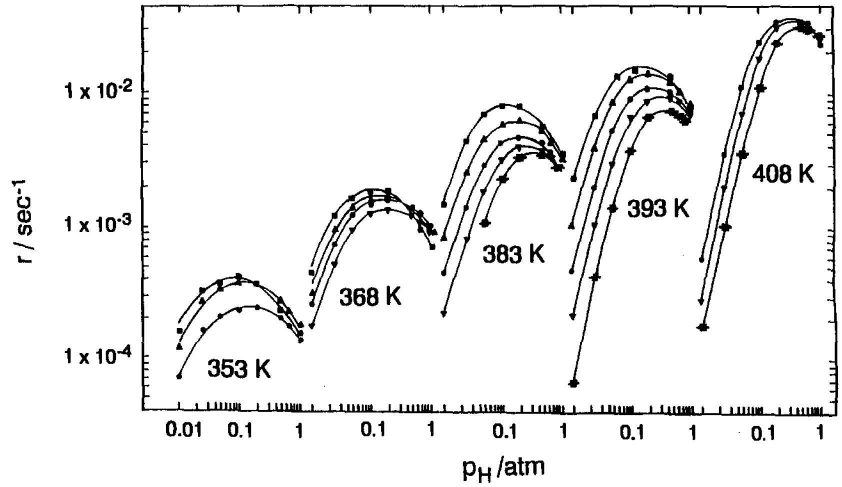

Fig. 1. Rate of hydrogenolysis of methylamine to methane and ammonia on a rhodium catalyst in the temperature range 353–408 K as a function of hydrogen partial pressure p_H for a series of different partial pressures of methylamine. The catalyst consisted of rhodium clusters dispersed on silica with a rhodium content of 1 wt% and a metal dispersion (ratio of surface Rh atoms to total Rh atoms) of 1.0. The rate r is given in molecules per second per surface rhodium atom (units shown simply as s^{-1} in the ordinate). Each of the different symbols used for data points represents data at a given level of methylamine partial pressure: (■) 0.0014–0.0018 atm; (▲) 0.0040–0.0042 atm; (●) 0.011–0.012 atm; (▼) 0.028–0.032 atm; (-■-) 0.072–0.085 atm.

different level of methylamine pressure. Curves are shown for a number of temperatures in the range of 353–408 K. The data are also presented in table 1. The ranges of methylamine and hydrogen partial pressures covered are 0.0014–0.085 atm and 0.010–1.0 atm, respectively. Rates were obtained at low conversions, with more than 95% of the data being obtained at conversions lower than 10%.

The curves in fig. 1 exhibit a characteristic pattern in which the rate passes through a maximum as the hydrogen partial pressure is increased over the range from 0.010 to 1.0 atm. At a given temperature, the position of the maximum is shifted slightly in the direction of higher hydrogen pressure when the methylamine partial pressure is increased over a wide range. Of particular interest is the finding that the rate increases with decreasing methylamine pressure over a broad range of hydrogen pressures covered in the investigation. As the hydrogen pressure increases, this inverse dependence of the rate on methylamine pressure becomes less pronounced and eventually disappears at a sufficiently high hydrogen pressure. Thus, the curves representing the dependence of reaction rate on hydrogen partial pressure for a series of fixed methylamine partial pressures appear to converge to a common curve at hydrogen pressures just beyond those corresponding to the rate maxima.

All of the features in the data which have just been described are incorporated in the empirical rate expression

$$r = kp_{\mathrm{H}}[1 + ap_{\mathrm{H}} + (bM)^{1/2}]^{-2}, \tag{3}$$

where M is the ratio $p_{\mathrm{M}}/p_{\mathrm{H}}$ of the partial pressures of methylamine and hydrogen. The parameters k, a, and b are given by the expressions (with $R = 1.99$ cal mol^{-1} deg^{-1})

$$k = 4.7 \times 10^5 \exp(-11000/RT)\,\mathrm{s}^{-1}\,\mathrm{atm}^{-1},$$

$$a = 2.8 \times 10^{-5} \exp(9600/RT)\,\mathrm{atm}^{-1},$$

$$b = 2.9 \times 10^{-3} \exp(5300/RT).$$

Eq. (3) with these values for the parameters fits the data reasonably well over virtually the whole range of conditions encompassed by the investigation, as shown in fig. 2. The quality of fit is poorest at the lowest temperature studied, 353 K.

At hydrogen partial pressures somewhat higher than those at which the rate maxima are observed, several of the curves in fig. 1 appear to cross, so that the effect of methylamine partial pressure on the reaction rate changes from an inverse dependence to a positive dependence. In particular, this change is observed at the lowest temperatures of the investigation, and is not accounted for by eq. (3). It would appear that the hydrogen pressure at which such a change becomes evident increases with increasing temperature.

4. Discussion

For a number of metals, Kemball and co-workers have shown that the exchange of deuterium with the hydrogen atoms in methylamine occurs more readily than

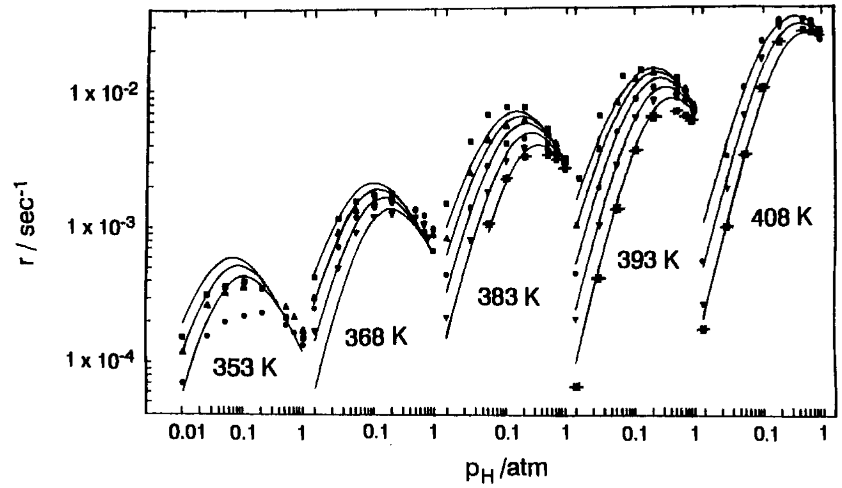

Fig. 2. Curves showing the fit of eq. (3) in the text to the rate data of fig. 1.

Table 1
Rate data for methylamine hydrogenolysis on a rhodium catalyst [a]

T	p_M	p_H	$10^5 \times r$	p_M	p_H	$10^5 \times r$	p_M	p_H	$10^5 \times r$	p_M	p_H	$10^5 \times r$	p_M	p_H	$10^5 \times r$
353	0.0014	0.010	15	0.0040	0.010	12	0.011	0.010	7						
		0.025	32		0.025	26		0.025	16						
		0.050	36		0.050	33		0.050	20						
		0.10	40		0.10	36		0.10	22						
		0.20	36		0.20	36		0.20	24						
		0.50	23		0.50	27		0.50	20						
		0.70	–		0.70	22		0.70	17						
		1.00	16		1.00	18		0.99	14						
368	0.0018	0.010	43	0.0040	0.010	31	0.012	0.010	26	0.032	0.010	17			
		0.025	120		0.025	93		0.025	72		0.025	51			
		0.050	160		0.050	130		0.050	120		0.050	92			
		0.10	180		0.10	150		0.10	140		0.10	120			
		0.20	180		0.20	160		0.20	150		0.20	130			
		0.50	120		0.50	120		0.50	140		0.50	130			
		0.70	93		0.70	100		0.70	120		0.70	110			
		1.00	69		1.00	87		0.99	97		0.97	94			
383	0.0018	0.010	140	0.0042	0.010	80	0.012	0.010	44	0.029	0.010	22	0.072	0.010	–
		0.025	400		0.025	240		0.025	130		0.025	80		0.025	–
		0.050	640		0.050	420		0.050	270		0.050	180		0.050	100
		0.10	730		0.10	530		0.10	390		0.10	300		0.10	220
		0.20	730		0.20	580		0.20	430		0.20	360		0.20	310
		0.50	510		0.50	480		0.50	390		0.50	340		0.50	320
		0.70	390		0.70	390		0.70	340		0.70	310		0.70	310
		1.00	270		1.00	300		0.99	260		0.97	270		0.93	260

Table 1 (Continued.)

T	p_M	p_H	$10^5 \times r$	p_M	p_H	$10^5 \times r$	p_M	p_H	$10^5 \times r$	p_M	p_H	$10^5 \times r$	p_M	p_H	$10^5 \times r$
393	0.0016	0.011	220	0.0040	0.010	100	0.012	0.010	45	0.028	0.010	21	0.077	0.010	7
		0.025	620		0.025	360		0.025	190		0.025	100		0.025	41
		0.062	1200		0.050	780		0.050	480		0.050	280		0.050	130
		0.12	1300		0.10	1100		0.10	830		0.10	610		0.10	350
		0.20	–		0.20	1300		0.20	1000		0.20	820		0.20	610
		0.50	1100		0.50	1100		0.50	940		0.50	860		0.50	670
		0.70	930		0.70	970		0.70	810		0.70	810		0.70	620
		1.00	680		1.00	760		0.99	650		0.97	700		0.92	570
408	0.011	0.010	56	0.032	0.010	27	0.085	0.010	17						
		0.025	320		0.025	190		0.025	97						
		0.050	1000		0.050	640		0.050	320						
		0.10	2200		0.10	1600		0.10	990						
		0.20	3100		0.20	2900		0.20	2100						
		0.50	3100		0.50	3200		0.50	2800						
		0.70	2800		0.70	3000		0.70	2700						
		0.99	2000		0.97	2500		0.92	2700						

[a] Column headings: T, temperature (K); p_M, methylamine partial pressure (atm); p_H, hydrogen partial pressure (atm); r, reaction rate (s^{-1}).

the hydrogenolysis of the carbon–nitrogen bond in the molecule, i.e., the exchange occurs at temperatures lower than those required for hydrogenolysis [1,4]. Thus, on the metal surface a hydrogen atom is released from, or added to, the carbon–nitrogen skeleton of the methylamine molecule at a rate which is substantially higher than the rate of the hydrogenolysis reaction. Therefore, it is reasonable to postulate that hydrogenolysis proceeds via a hydrogen deficient intermediate formed in the chemisorption of methylamine on the metal surface. Scission of the carbon–nitrogen bond in such an intermediate produces two hydrogen deficient surface fragments, one containing carbon and the other containing nitrogen. Hydrogenation of these fragments yields methane and ammonia as the reaction products. The general mechanistic features of the reaction are similar to those which have commonly been proposed for the hydrogenolysis of the carbon–carbon bond in ethane and other alkanes [5–8].

The kinetics of hydrogenolysis of methylamine on rhodium are complex, as demonstrated by the data obtained in the present investigation on the dependence of the rate on the partial pressures of hydrogen and methylamine. The complexity is, in part, attributable to the wide range of partial pressures covered in the investigation. When the hydrogen partial pressure is varied by two orders of magnitude at a fixed methylamine partial pressure, the rate of hydrogenolysis passes through a maximum. This is observed regardless of the fixed value of methylamine pressure employed in the range of 0.0014–0.085 atm, another variation approaching two orders of magnitude. There is also limited evidence, especially at the lowest temperatures, that the rates pass through a maximum when the methylamine partial pressure is varied at a fixed partial pressure of hydrogen.

This type of behavior is characteristic of a bimolecular surface reaction between two chemisorbed species, each of which is in equilibrium with a reactant molecule in the gas phase [9,10]. However, in this type of situation, the partial pressure of one reactant giving a maximum rate is expected to be a sensitive function of the partial pressure of the other reactant [10], at least when the latter is in a range where an increase in its value has an adverse effect on the rate (an indication that its coverage of the active catalyst surface is substantial). In the present investigation, however, we do not observe this sort of behavior. As the data in fig. 1 show, the hydrogen partial pressure at which the rate passes through a maximum is not a sensitive function of methylamine partial pressure, the former varying at most by a factor of three when the latter is varied by two orders of magnitude.

Alternatively, the complexity introduced by the wide range of reactant partial pressures investigated may be an indication of a change in the nature of the rate determining step of the reaction. In discussing the kinetic data from this point of view, we begin by representing a hydrogen deficient surface intermediate by the formula CH_xNH_y(ads), where (ads) stands for adsorbed species. We then write the following type of step for the scission of the carbon–nitrogen bond:

$$CH_xNH_y(\text{ads}) + S \rightarrow CH_x(\text{ads}) + NH_y(\text{ads}), \qquad (4)$$

where S represents a vacant surface site and the subscripts x and y in the formulas of the surface species indicate that the number of hydrogen atoms bonded to the carbon and nitrogen atoms are unknown and therefore unspecified. For our purposes here, S could be a single metal atom or perhaps a pair of such atoms. The interaction of the surface intermediate with a neighboring vacant site is shown for the purpose of generality in the subsequent discussion, since the participation of a vacant site in such a step is a reasonable possibility [11].

At the highest hydrogen partial pressures of the investigation (beyond the rate maxima), where the rate exhibits an inverse dependence on hydrogen pressure and a zero order or even slightly positive dependence on methylamine pressure, we suggest that the rate limiting step is the one in which scission of the carbon–nitrogen bond occurs, i.e., a step such as that depicted in eq. (4). The inverse dependence of the reaction rate on hydrogen partial pressure could then arise because an increase in hydrogen pressure decreases the concentration of the intermediate CH_xNH_y(ads) and/or the concentration of vacant sites. Such effects have commonly been proposed in discussions of the kinetics of ethane hydrogenolysis on metals [12–15].

On the other hand, at the lowest hydrogen partial pressures of the investigation (well below those at which the rate maxima are observed), where the rate exhibits a positive dependence on hydrogen pressure and an inverse dependence on methylamine pressure, we suggest that the rate limiting step is one in which chemisorbed hydrogen participates directly as a reactant. For example, the reaction of chemisorbed hydrogen with the surface species CH_x(ads) and NH_y(ads) could be rate limiting. We do not specify the nature of the chemisorbed hydrogen, i.e., atomic or molecular. The inverse dependence of the rate on the methylamine pressure, coupled with the positive dependence on hydrogen pressure, suggests that the active catalyst surface is covered to a significant extent by a species such as CH_xNH_y and to a much lower extent by hydrogen. Under such conditions, an increase in hydrogen pressure can increase the concentration of vacant sites on the surface by decreasing the concentration of CH_xNH_y. The concentration of chemisorbed hydrogen can then show a stronger dependence on hydrogen pressure than would be expected if methylamine were not present in the system. This could provide an explanation for the strong dependence of the rate on hydrogen partial pressure which is particularly apparent at the higher temperatures and higher methylamine partial pressures in fig. 1.

Thus, a reasonable interpretation of the complex kinetics can be made in terms of different types of rate determining steps at the extremes of low and high hydrogen partial pressures. In our analysis of the rate data, we have concluded that various kinetic schemes based on a single rate determining step for the whole range of variables investigated do not provide an adequate quantitative description of the main features of the data or are questionable from a mechanistic standpoint. A kinetic treatment of a sequence of steps which is complete enough to provide a sufficiently general rate equation allowing for changes in rate determining steps has not been made, but we have presented an empirical rate equation with a characteristic kinetic form that fits virtually the whole range of data obtained in the investigation. Such a rate equation is useful because it describes a complex set of data over a wide range of conditions. As Boudart and Djéga-Mariadassou [16] point out in the Introduction of their excellent book, Kinetics of Heterogeneous Catalytic Reactions, the first objective of the kineticist is to provide a quantitative description of the rate of the chemical change, whatever may be the underlying mechanism. The potential value of good kinetic data and a working rate expression may not be completely evident at the time of the investigation. Thus, they may contribute valuable insight at some future time, possibly as a result of the acquisition of new information of a different kind. In the present case, such new information might include spectroscopic identification of surface species that could conceivably be present during the reaction, as well as kinetic data on possible elementary steps. Such thermodynamic information as the strength of the nitrogen–metal and carbon–metal bonds at the catalyst surface would also be helpful. In combination with such information, the data of the present investigation could be very useful for a microkinetic analysis of the type which has been described by Dumesic et al. [17].

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