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## Research Article

# Gas-Phase Photocatalytic Oxidation of Dimethylamine: The Reaction Pathway and Kinetics

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Gas-phase photocatalytic oxidation (PCO) and thermal catalytic oxidation (TCO) of dimethylamine (DMA) on titanium dioxide was studied in a continuous flow simple tubular reactor. Volatile PCO products of DMA included ammonia, formamide, carbon dioxide, and water. Ammonia was further oxidized in minor amounts to nitrous oxide and nitrogen dioxide. Effective at 573 K, TCO resulted in the formation of ammonia, hydrogen cyanide, carbon monoxide, carbon dioxide, and water. The PCO kinetic data fit well to the monomolecular Langmuir-Hinshelwood model, whereas TCO kinetic behaviour matched the first-order process. No deactivation of the photocatalyst during the multiple long-run experiments was observed.

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## 1. INTRODUCTION

The chemical, pharmaceutical, and petrochemical industries are among sources producing waste streams containing organic nitrogen-containing compounds. Dimethylamine (DMA) is used as a dehairing agent in tanning, in synthesis of dyes, rubber accelerators, pharmaceuticals, soaps, and cleaning compounds, and as a fungicide. Dimethylamine also appears to be a decomposition or photocatalytic oxidation (PCO) by-product of complex amino compounds, such as, for example, unsymmetrical dimethylhydrazine ((CH<sub>3</sub>)<sub>2</sub>N-NH<sub>2</sub>, UDMH), an eco-toxicant of great concern used mostly as a component of rocket propellants [1]. The present research is a part of a broader study targeting the disclosure of the reaction pathways in PCO of UDMH.

A common abatement of air pollution practice is incineration, which, for nitrogen-containing compounds, may result in the formation of nitrogen oxides, contributing to the formation of photochemical smog, the greenhouse effect, and stratospheric ozone depletion. To mitigate these unwanted environmental effects, selective noncatalytic and catalytic treatment processes have been required in order to reduce NO<sub>x</sub> emissions [2]. Photocatalytic oxidation (PCO) on titanium dioxide may present a potential alternative to incineration as it has advantages such as the ambient conditions at which the PCO reaction proceeds effectively although higher temperatures may be also applied.

Earlier [3], we have studied the PCO and thermal catalytic oxidation (TCO) of methylamine (MA) on titanium dioxide since this substance is another possible PCO product of UDMH. The PCO products of MA included ammonia, minor amount of nitric oxides (NO<sub>2</sub> and N<sub>2</sub>O), water, and carbon dioxide formed presumably from formic acid as an intermediate carbonaceous oxidation by-product. We have shown also that the thermal decomposition of methylamine (MA) proceeded along two reaction pathways: dehydrogenation of the MA molecule with hydrogen cyanide formed as a product through the stage of methanimine formation, and C-N bond scission forming ammonia and the carbon mineralization products. The formation of cyanide was also observed in [4], where the thermal decomposition of DMA adsorbed on an Si (100) surface was studied; at low concentrations, DMA decomposed to hydrogen and hydrogen cyanide as major products, or to hydrogen and imine dehydrogenation products at higher concentrations. The difference between the products of TCO and PCO may, therefore, lead to an application of PCO as a safer amino compounds' abatement method compared to thermal decomposition or incineration.

## 2. EXPERIMENTAL METHODS

The gas-phase PCO of DMA over UV-illuminated TiO<sub>2</sub> was studied using an annular photocatalytic reactor having an

inner diameter of 32 mm. The reactor's length was 165 mm and the total volume of the empty space of the reactor was 55 mL. The annular gap between the wall of the lamp and the inner wall of the reactor was 3.5 mm. A 365 nm, 15 W low-pressure mercury UV lamp (Sylvania, UK) was positioned coaxially in the reactor; the diameter of the lamp was 25 mm. The preliminary experiments carried out with no TiO<sub>2</sub> catalyst applied showed that the 365 nm light did not exhibit an activity in decreasing DMA concentration in gaseous phase.

The inner wall of the reactor was coated with TiO<sub>2</sub> (Degussa P25) by rinsing with a TiO<sub>2</sub> aqueous suspension, repeated 25 times, and each rinse was followed by drying. The reactor was assembled with the lamp after the catalyst had been attached to the reactor's wall. Approximately, 0.3 g of TiO<sub>2</sub> coated about 197 cm<sup>2</sup> of the reactor (1.5 mg cm<sup>-2</sup>). The irradiance of the UV-lamp was measured with a UVX Radiometer at a distance of 3.5 mm from the lamp and averaged about 3.8 mW/cm<sup>-2</sup>. The reactor was used in a continuous flow mode.

In the experiments, an evacuated gas cylinder was first filled with the desired amount of gaseous DMA (Fluka) through an injection port, and then filled with synthetic air (20% O<sub>2</sub>, 80% N<sub>2</sub>). The air stream containing DMA was blended with diluent gas to deliver the desired volatile organic compound concentration to the reactor. The temperature in the reactor during the PCO reactions was maintained at 353 and 413 K. The temperature was adjusted with a heating tape wrapped around the reactor. The tape was controlled with a temperature regulator, Omega CN 9000A, with a K-type thermocouple. The temperature deviations did not exceed ±1 K.

The gas flow rate was 3.03 L min<sup>-1</sup>, which made the contact time equal to 1.1 seconds. This contact time was sufficient to reliably register the difference between DMA concentrations in the inlet and outlet streams, keeping that difference within 30 to 60% limits. The reaction products were analysed by a Perkin Elmer 2000 FT-IR spectrometer equipped with a Sirocco 10.6 m gas cell. Inlet concentrations of DMA varied from 50 to 170 ppmv (2.2 · 10<sup>-3</sup> to 7.6 · 10<sup>-3</sup> mol L<sup>-1</sup>). No humidity was introduced to the air stream.

The experiments on thermal catalytic decomposition of DMA were conducted in the dark at 573 K. At lower temperatures no measurable decrease in DMA concentration was observed. The total volume of the reactor was increased to 0.105 L, which, at a gas flow rate of 3.03 L min<sup>-1</sup>, made the contact time as long as 2.1 seconds.

### 3. RESULTS AND DISCUSSION

#### 3.1. PCO and TCO products

The PCO volatile products, visible in the infrared spectra of the outlet gas stream at the contact time of 1.1 seconds, include ammonia, formamide, carbon dioxide, and water. To see the evolution of the products with the contact time extension, the contact time was increased to 2.1 and 4.5 seconds with decreasing the gas flow rate. Longer contact time resulted in deeper oxidation of DMA showing the formation

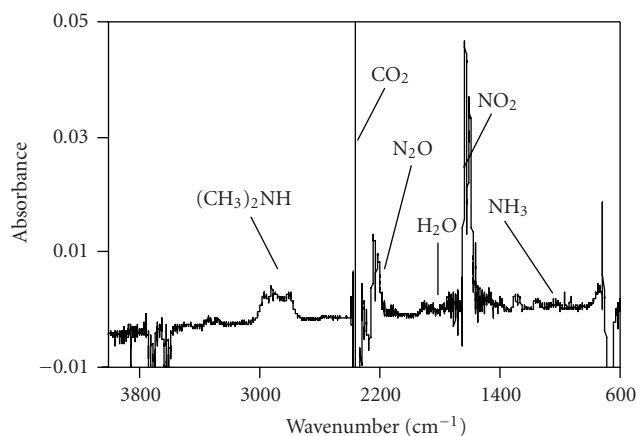


FIGURE 1: FT-IR spectrum of the outlet flow during PCO of DMA at a contact time of 4.5 seconds.

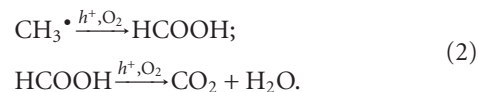
of nitrogen dioxide, nitrous oxide, carbon dioxide, and water. Ammonia peaks decreased with increasing the contact time.

Formation of nitrous oxide N<sub>2</sub>O in PCO of ammonia was described by Pérez-Ramírez et al. [5] as a result of interaction of ammonia and nitrogen oxide (NO). Similarly, PCO of DMA resulted in the formation of ammonia, which further was most likely oxidized to NO. Nitrogen oxide was partially oxidized further to nitrogen dioxide (NO<sub>2</sub>) and partially reacted with residual ammonia forming nitrous oxide (N<sub>2</sub>O). Nitrogen oxide (NO) was not seen among the reaction products due to its high reactivity.

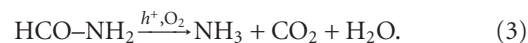
The reaction trends, therefore, could be described by the following sequence of reactions. The adsorbed DMA molecule, first, is oxidised with the positively charged hole, resulting in the formation of formamide and reactive methyl radical:



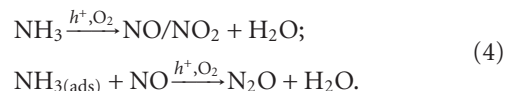
The latter reacts fast with oxygen forming formic acid. Formic acid is mineralized fast, giving carbon dioxide and water:



Formamide further is oxidized to carbon dioxide, water, and ammonia:



Ammonia is partially oxidized to nitrogen oxide, which reacts producing nitrogen dioxide and nitrous oxide in reaction with residual ammonia:



The thermal catalytic oxidation (TCO) experiments with DMA in the dark were carried out at 573 K. The volatile

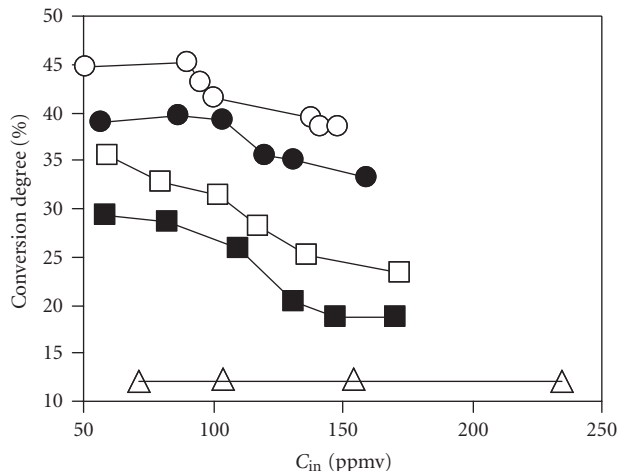


FIGURE 2: Conversion of DMA versus inlet concentration in PCO at (■) 353 K, (□) 373 K, (●) 393 K, and (○) 413 K, and TCO at (△) 573 K.

products leaving the reactor included ammonia, hydrogen cyanide, carbon dioxide, and water. Thus the TCO of DMA proceeded along two reaction pathways: dehydrogenation of the DMA molecule with hydrogen cyanide formed as a product most likely through the methanimine stage, and C–N bond scission forming ammonia and the carbon mineralization products. The similar products of the reaction were observed earlier with the TCO of MA at 573 K [3].

### 3.2. PCO and TCO kinetics

As previously established by Kim and Hong [6], the complex mechanisms of photocatalytic reactions is difficult to describe for an extended reaction time in a simple model. Therefore, the kinetic modelling is usually restricted to the analysis of the initial rate of photocatalytic degradation. This can be obtained from a minimum detectable conversion of the reactant at a minimum contact time.

The Langmuir-Hinshelwood (L-H) model of the monomolecular reaction kinetics, the reciprocal form of which is presented by (5), has been widely used for the description of gas-phase photocatalytic reactions:

$$\frac{1}{r_0} = \frac{1}{kK} \frac{1}{C_0} + \frac{1}{k}, \quad (5)$$

where  $r_0$  is the initial reaction rate ( $\text{mol m}^{-3} \text{s}^{-1}$ ),  $C_0$  is the inlet concentration of the reactant ( $\text{mol m}^{-3}$ ),  $k$  is the reaction rate constant ( $\text{mol m}^{-3} \text{s}^{-1}$ ), and  $K$  is the Langmuir adsorption coefficient ( $\text{m}^3 \text{mol}^{-1}$ ).

Figure 2 shows the conversion of DMA in PCO versus its inlet concentration: the conversion varies inversely with the inlet concentration at the tested temperatures, that is, the process is obviously not of the first order and may fit to the L-H description.

The initial rate of PCO of DMA was observed to fit well to the L-H kinetic model: a linear plot of  $r_0^{-1}$  versus  $C_0^{-1}$

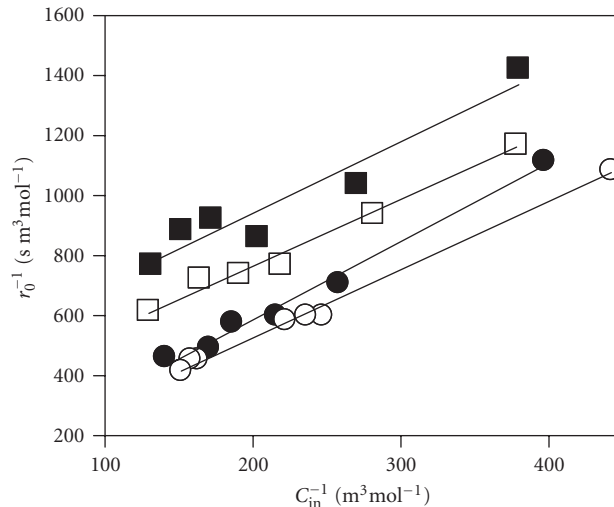


FIGURE 3: Reciprocal PCO reaction rates on  $\text{TiO}_2$  versus the reciprocal DMA initial concentrations at (■) 353, (□) 373, (●) 393, and (○) 413 K.

(5) is shown in Figure 3, from which,  $k$  and  $K$  values were obtained. Reaction rate constants and the Langmuir adsorption coefficients for PCO of DMA at the tested temperatures are given in Table 1.

One can see the reaction rate constant increasing and the adsorption coefficient decreasing with increasing the temperature, making the apparent reaction rate practically independent of the temperature within the tested range. The new data on PCO of MA kinetics as compared to [3] was obtained on course of the present research and presented in Table 1. One can see that reaction rate constants  $k$  for PCO of MA are higher than that for DMA at a temperature range from 353 to 373 K, although DMA showed better adsorption than MA at these temperatures. As a result, the apparent reaction rate of MA exceeded the one of DMA for about 2.5 times. However, the reaction rate constant for MA seemed to be less sensitive to temperature than that for DMA, increasing faster with increasing the temperature; the similar trend was observed with the Langmuir adsorption coefficient, decreasing more dramatically for DMA with the temperature growth than for MA. Nevertheless, the apparent reaction rate constant  $kK$  remained practically constant for both substances within the tested temperature range.

In contrast to PCO, TCO kinetic behaviour indicated the first-order process: the conversion degree varied proportionally with the inlet concentration of DMA at 573 K (Figure 2). A similar result was observed in an early study with the TCO of MA [3].

No sign of photocatalyst deactivation was observed in more than 100 experimental runs of 2 hours each, which also was observed earlier with MA and explained [7] by the minor amount of nitric acid formed in the PCO of amino compounds. The presence of additional methyl group in the DMA molecule did not add carbonaceous products able to deactivate the photocatalyst. The authors attempted to identify nitrite/nitrate by means of ionic chromatography in

TABLE 1: Reaction rate constants and Langmuir adsorption coefficients for PCO of DMA and MA on TiO<sub>2</sub>

| Temperature (K) | DMA   |   | MA  |   |
|-----------------|---|---|---|---|
|                 | $k$ (mmol m <sup>-3</sup> s <sup>-1</sup> ) | $K$ (m <sup>3</sup> mol <sup>-1</sup> ) | $k$ (mmol m <sup>-3</sup> s <sup>-1</sup> ) | $K$ (m <sup>3</sup> mol <sup>-1</sup> ) |
| 353             | 2.2 ± 0.1                                   | 193 ± 1                                 | 6.6 ± 0.1                                   | 148 ± 1                                 |
| 373             | 3.1 ± 0.1                                   | 147 ± 1                                 | 8.7 ± 0.1                                   | 125 ± 1                                 |
| 393             | 15.0 ± 0.1                                  | 26 ± 1                                  | 10.5 ± 0.1                                  | 93 ± 1                                  |
| 413             | 16.0 ± 0.1                                  | 25 ± 1                                  | 12.5 ± 0.1                                  | 77 ± 1                                  |

TABLE 2: Arrhenius equation parameters for the PCO of DMA and MA.

| Temperature range | Parameter   | DMA                     | MA        |
|-------------------|---|-------------------------|-----------|
| 353 to 413 K      | $\Delta H$ , kJ mol <sup>-1</sup>                   | -42 ± 1                 | -14 ± 1   |
|                   | $A_{\text{ads}}$ , m <sup>3</sup> mol <sup>-1</sup> | 1.25 · 10 <sup>-4</sup> | 1.5 ± 0.5 |
|                   | $E$ , kJ mol <sup>-1</sup>                          | 42.1 ± 1                | 13 ± 1    |
|                   | $A_r$ , mol m <sup>-3</sup> s <sup>-1</sup>         | 0.35 · 10 <sup>4</sup>  | 0.5 ± 0.5 |

water used for rinsing the catalyst after a few experimental runs but failed to see these anions above the detection limit.

### 3.3. Thermodynamics of PCO

The dependence of the L-H kinetic parameters, the reaction rate constant, and the Langmuir adsorption coefficient on temperature was analyzed in the form of Arrhenius equations:

$$\begin{aligned} k &= A_r e^{-E/RT}; \\ K &= A_{\text{ads}} e^{-\Delta H/RT}, \end{aligned} \quad (6)$$

where:  $A_r$  and  $A_{\text{ads}}$  are pre-exponential factors for the reaction rate constant and the adsorption coefficient, mol m<sup>-3</sup> s<sup>-1</sup> and m<sup>3</sup> mol<sup>-1</sup>, respectively,  $E$  and  $\Delta H$  the activation energy of the reaction and the adsorption enthalpy, kJ mol<sup>-1</sup>, respectively,  $R$  the universal gas constant, kJ mol<sup>-1</sup> K<sup>-1</sup>, and  $T$  the temperature, K.

The values of the pre-exponential factors, the activation energy of the reaction, and the adsorption enthalpy determined in the present study are given in Table 2. The PCO rate constant for DMA appears to be more sensitive to temperature within the tested range than for MA since it has larger Arrhenius equation parameters.

## 4. CONCLUSIONS

Dimethylamine is easily oxidized photocatalytically on UV-irradiated TiO<sub>2</sub>. The volatile PCO products of DMA included ammonia, formamide, carbon dioxide, and water. TCO resulted in the formation of ammonia, hydrogen cyanide, carbon monoxide, carbon dioxide, and water. The PCO reaction kinetics fitted satisfactorily to the Langmuir-Hinshelwood description. The photocatalyst demonstrated stable activity at temperature and concentration ranges tested in the experiments. No toxic cyanide is formed in the PCO reactions.

## ACKNOWLEDGMENTS

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