

## A kinetic study on the electrochemical hydrogenation of *N,N*-dimethylformamide to trimethylamine

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The preparation of amines from amides is an important reaction that is widely used in pharmaceutical and industrial chemistry. A simple, convenient, and effective method for the selective electrochemical hydrogenation of *N,N*-dimethylformamide (DMF) to trimethylamine (TMA) was developed. The effects of the absence and presence of water, temperature, and scanning rate were discussed regarding the electrocatalytic reduction of DMF using cyclic voltammetry, and the polarization curves at different temperatures also examined. The results indicated that electrochemical hydrogenation of DMF to TMA took place on a copper cathode, with water providing protons for the reaction, that effect changed the basic electrolyte properties, such as viscosity and density, which increased the reaction rate, such that increased reaction temperature improved the copper electrode electrochemical activity. The reduction process for DMF was controlled by diffusion at the reaction site and the diffusion coefficient ( $D_0$ ) was  $1.09 \times 10^{-9}$  cm/s and the apparent activation energy of DMF reduction using a copper cathode at 21.03 kJ/mol.

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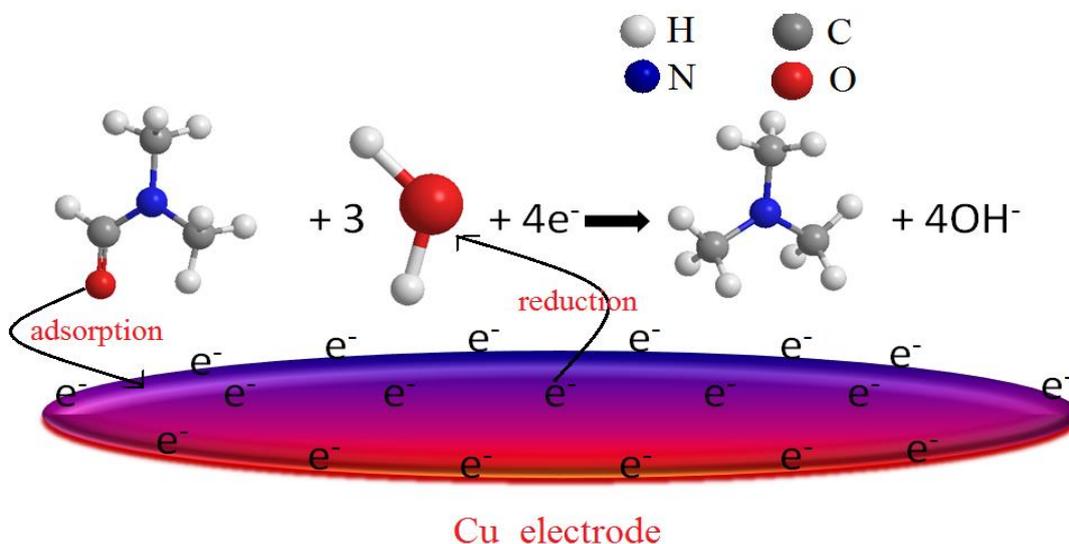
**Keywords:** *N,N*-Dimethylformamide, Trimethylamine, Electro-organic synthesis, Selective hydrogenation

### 1. INTRODUCTION

Electrochemistry has emerged as a powerful tool in organic synthesis methods [1, 2]. The reducing or oxidizing capacity in electrolysis is controlled by the voltage applied to galvanic cells. No external chemical oxidants or reductants are required. Two methods have been mainly used for preparative electrolysis, constant-current and controlled-potential electrolysis, and electrochemical methods are often only considered after all other methods have been exhausted [3-5]. Meanwhile, methylamine, dimethylamine, and trimethylamine (MMA, DMA, and TMA, respectively) are

important industrial chemical intermediates, with an annual worldwide output of  $\sim 1.8 \times 10^9$  lbs/yr. TMA is widely used in the synthesis of fine and special chemicals, such as synthetic drugs, pesticides, or surfactants [6, 7]. More importantly, the N-CH<sub>3</sub> group is a common functional group in organic compounds, existing in drugs, natural products, nitrogen bases, and dyes [8-10]. The catalytic activation of C-N bonds is very important in organic chemistry, especially in the synthesis of nitrogen-containing compounds [11-14]. In 1884, a method for synthesizing TMA from ammonia (NH<sub>3</sub>) and methanol (CH<sub>3</sub>OH) was first reported using zinc chloride (ZnCl<sub>2</sub>) as a dehydrating agent [15]. Other early studies [16, 17] led to patents, the first of which was granted to DuPont [18]. TMA is mainly prepared by methanol amination in industrial settings, which occurs at approximately 390–430°C and  $\sim 5$  MPa. This reaction requires high temperature, high pressure, high energy, and sophisticated equipment [19, 20].

To the best of our knowledge, no study of the effects of temperature, scanning rate, or the presence or absence of water, have been discussed regarding the electrocatalytic reduction of *N,N*-dimethylformamide (DMF) by cyclic voltammetry. In this study, DMF was electrochemically hydrogenated to TMA using a copper cathode at room temperature and ambient pressure and the effects of the absence and presence of water, temperature, and scanning rate discussed regarding the electrocatalytic reduction of DMF by cyclic voltammetry. Scheme 1 shows the electrochemical reduction mechanism of DMF to TMA.



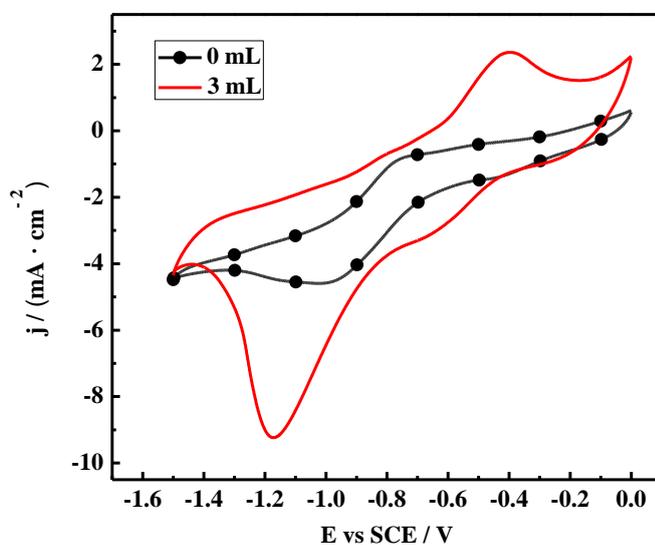
**Scheme 1.** The reaction mechanism of DMF to TMA.

## 2. EXPERIMENTAL SECTION

The details of the chemicals, instrumentation, and procedures as well as the analysis and characterization of the product were performed following a published protocol by Jia *et al.* [21]. The effects of the absence and presence of water, temperature, and scanning rate were discussed regarding the electrocatalytic reduction of DMF using cyclic voltammetry.

### 3. RESULTS AND DISCUSSION

The cyclic voltammogram of the copper electrode in DMF + 0.1 M  $(C_3H_7)_4NBF_4$  at a scan rate of  $30 \text{ mV}\cdot\text{s}^{-1}$  in the absence and presence of water (3 mL) showed no clear reduction peak on the copper electrode without adding water, which indicated that DMF was not reduced to TMA (Fig. 1). When water (3 mL) was added in DMF + 0.1 M  $(C_3H_7)_4NBF_4$ , a reduction peak for DMF was observed on the copper electrode (-1.15 V), which showed that copper exhibited a good catalytic effect and the current density significantly increased. This indicated that water was an important factor for the reduction of DMF to TMA. From a practical point of view, the electrochemical hydrogenation of DMF to TMA on the copper electrode could have reduced energy consumption when water was added and presence of  $H_2O$  increased the TMA yield. The surprising result from the copper electrode was its excellent selectivity of DMF to TMA in the presence of water, indicating the possible role of water in providing protons for converting DMF to TMA. Meanwhile, water changed the basic properties of the electrolyte, such as viscosity and density, thereby speeding up the reaction speed. At the same time, water reduced the aggregation of ion pairs in the electrolyte and thus accelerated electrolyte conductivity [22, 23].



**Figure 1.** Cyclic voltammetry recorded at  $\nu = 30 \text{ mV s}^{-1}$  in DMF+ 0.1 M  $(C_3H_7)_4NBF_4$  in the absence and presence of 3 mL  $H_2O$  on Cu electrode

The synthesis of TMA from DMF on a copper cathode was further studied by controlled-potential electrolyses in DMF + 0.1M  $(C_3H_7)_4NBF_4$  and DMF + 0.1M  $(C_3H_7)_4NBF_4 + H_2O$  (Table 1). However, DMF was not reduced in DMF + 0.1M  $(C_3H_7)_4NBF_4$ . The main reduction products were TMA (83.0%) and  $CO_2$  (10%) in DMF + 0.1M  $(C_3H_7)_4NBF_4 + H_2O$ .

**Table 1.** Electrolysis data for DMF to TMA<sup>a</sup>

Entry	Temp K	Solvent	Cathode	E <sub>app</sub> <sup>b</sup> V	j <sup>c</sup> mA/cm <sup>2</sup>	Conv %	C <sub>3</sub> H <sub>9</sub> N %	CO <sub>2</sub> %	CE <sup>d</sup> %
1	293	DMF	Cu	-1.15	4.82	0	0	0	0
2	293	DMF/H <sub>2</sub> O	Cu	-1.15	9.25	96.0	83.0	10	56
3	303	DMF/H <sub>2</sub> O	Cu	-1.15	12.28	96.5	84.1	12	43
4	313	DMF/H <sub>2</sub> O	Cu	-1.15	14.00	96.8	85.2	14	45
5	323	DMF/H <sub>2</sub> O	Cu	-1.15	15.19	97.1	85.9	14	50

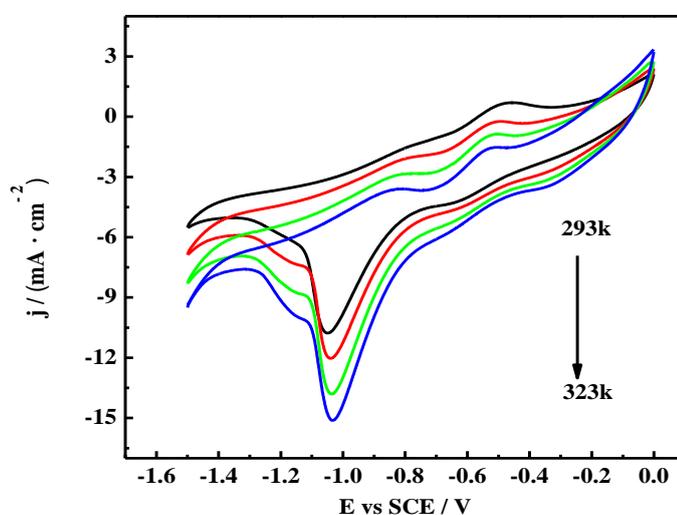
<sup>a</sup>Yields were calculated with on the basis of DMF.

<sup>b</sup>Applied potential respect to SCE.

<sup>c</sup>Average current densities.

<sup>d</sup>Current efficiency, theoretical charge for product formation/experimental charge.

The impact of temperature variation on DMF reduction on a copper electrode was investigated by recording cyclic voltammograms at different temperatures, including 293, 303, 313, and 323 K, in DMF + 0.1M (C<sub>3</sub>H<sub>7</sub>)<sub>4</sub>NBF<sub>4</sub> + H<sub>2</sub>O (3 mL). The voltammogram shape remained unchanged at different temperatures (Fig. 2). However, as the temperature increased from 293 to 323 K, the reduction peak current displacement of DMF on the copper electrode surface reached a lower potential and the peak current significantly increased. This indicated that the reduction reaction current increased with increased temperature. These results indicated that the electrochemical activity of the copper electrode increased at higher temperatures. This might have been because DMF had a very high viscosity, which restricted free ion movement, resulting in lowered conductivity and reaction rate. With increased temperature, the electrolyte viscosity decreased, such that the per unit volume of the electrolyte conductive ions gradually increased and the rate of movement of free ions gradually accelerated. Thus, raising the temperature enhanced conductivity and accelerated the reaction rate [24, 25].



**Figure 2.** Cyclic voltammograms in DMF + 0.1 M (C<sub>3</sub>H<sub>7</sub>)<sub>4</sub>NBF<sub>4</sub> + H<sub>2</sub>O on a copper electrode at different temperatures (293–323 K and  $\nu$  at 30 mV·s<sup>-1</sup>).

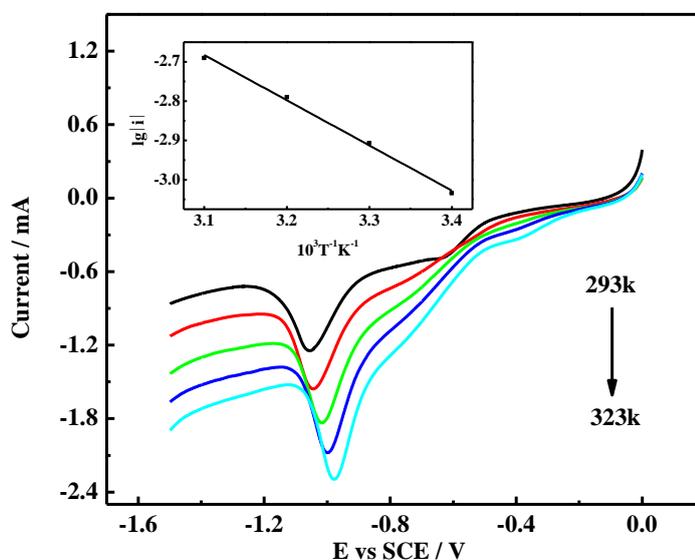
The electrochemical synthesis of TMA from DMF at a copper cathode was further studied by controlled-potential electrolysis in DMF + 0.1M (C<sub>3</sub>H<sub>7</sub>)<sub>4</sub>NBF<sub>4</sub> + H<sub>2</sub>O (3 mL) at different temperatures (Table 1). An improvement in TMA yield was observed with increased temperature, which indicated that the electrochemical activity of the copper electrode increased at higher temperatures.

Polarization curves of a copper electrode in DMF + 0.1M (C<sub>3</sub>H<sub>7</sub>)<sub>4</sub>NBF<sub>4</sub> + H<sub>2</sub>O (3 mL) at a fixed scan rate of 10 mV·s<sup>-1</sup> are shown in Figure 3 (inset shows the relationship of lg|i| and 1/T). The corresponding linear equation was

$$\lg|i| = 0.80 - 1.10 \frac{1}{T} \quad (1), R^2 = 0.995$$

$$\text{According to equation: } \lg|i| = a + \frac{b}{T} \text{ and } b = -\frac{E_a}{2.3R}$$

where  $i$  is the current,  $T$  the temperature,  $a$  and  $b$ , constants,  $R$  the gas constant, and  $E_a$  the reaction apparent activation energy. The  $E_a$  of DMF reduction using a copper cathode was expressed as equation (1), with  $E_a$  at 21.03 kJ/mol.



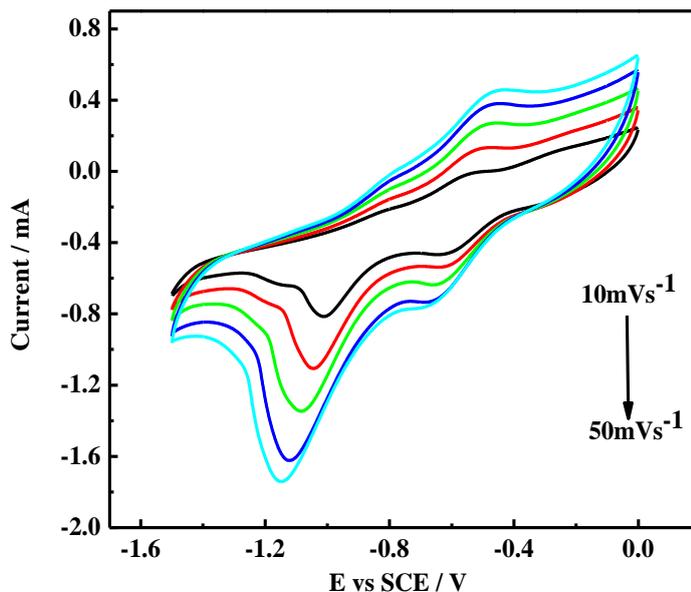
**Figure 3.** Polarization curves at different temperature (293 K–323 K and  $\nu$  at 10 mV·s<sup>-1</sup>. Inset, relationship of lg|i| and 1/T)

Under the condition of linear diffusion, irreversible peak current equation was deduced by Laplace conversion method [26, 27].

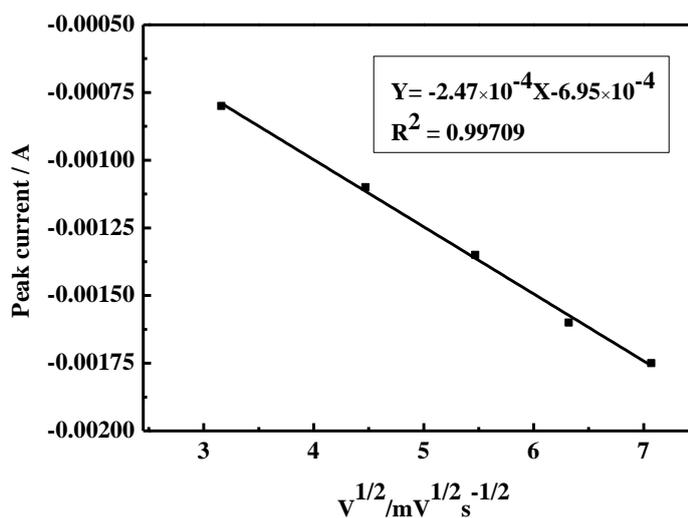
$$i_p = -(2.69 \times 10^5) n^{3/2} C_o^* D_o^{1/2} \nu^{1/2} \quad (298 \text{ K}) \quad (2)$$

Where  $i_p$  is the reduction peak current,  $n$  the number of transferred electrons of the overall reaction,  $D_o$  the diffusion coefficient,  $\nu$  the scan rate,  $C_o^*$  the initial reactant concentration. Cyclic voltammograms of a copper electrode in DMF + 0.1M (C<sub>3</sub>H<sub>7</sub>)<sub>4</sub>NBF<sub>4</sub> + H<sub>2</sub>O (3 mL) at various scan rates from 10 to 50 mV·s<sup>-1</sup> at 298 K showed that the DMF reduction peak increased and shifted to a lower potential as the scan rate increased, indicating that the electrochemical reduction DMF to TMA was irreversible (Fig. 4) [28, 29]. In addition, the analysis of the DMF reduction peak current as a function of scan rate indicated that the peak current was in a good linear relationship with the scan rate square root. This

was consistent with formula (1) and indicated that the DMF reduction process was controlled by diffusion at the reaction site (Fig. 5) [30, 31].



**Figure 4** Cyclic voltammograms in DMF+ 0.1 M  $(C_3H_7)_4NBF_4$ + 3 mL  $H_2O$  on copper electrode at different scan rates ( $10\text{--}50\text{ mV}\cdot\text{s}^{-1}$ ).



**Figure 5.** The relationship between  $i_p$  and  $v^{1/2}$

It took much less time to attain the same potential, such that, when the diffusion layer was thinner, the diffusion velocity was faster when the scan rate was increased, which was consistent with Figure 3. The value for  $D_0$  was  $1.09 \times 10^{-9}\text{ cm}\cdot\text{s}^{-1}$  from formula (2), in which  $D_0$  was much smaller due to high electrolyte viscosity.

#### 4. CONCLUSIONS

In conclusion, a new synthetic methodology was developed for producing TMA by electrochemical reduction of DMF using a copper cathode. The results indicated that water provided protons for the reaction and changed the electrolyte's basic properties, such as viscosity and density, which thus sped up the reaction rate. The electrochemical activity of the copper electrode was observed to increase at higher temperatures, such that the electrode process for DMF reduction was apparently controlled by diffusion at the reaction site. With  $D_0$  at  $1.09 \times 10^{-9} \text{ cm} \cdot \text{s}^{-1}$  from formula (2), the  $D_0$  was much smaller due to high electrolyte viscosity. The apparent  $E_a$  of DMF reduction using a copper cathode was obtained from equation (1), at  $21.03 \text{ kJ} \cdot \text{mol}^{-1}$ .

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