Electronic Supporting Information

Homogeneous synthesis of hydroxylamine hydrochloride via acid-catalyzed hydrolysis of nitromethane

Fanglin Huo and Yangcheng Lu*

The State Key Lab of Chemical Engineering, Department of Chemical Engineering, Tsinghua University, Beijing 100084, China

*Corresponding author email: luyc@tsinghua.edu.cn

Experimental conditions

The concentrations of HCl, water and NM for all kinetics experiments were listed in Table. S1 for fast query.

Table S1 Concentrations of NM, HCl and water of all kinetics experiments

Entry	Reactants concentration [a]
1	$C_{NM,0}$= 0.6 M, $C_{HCl,0}$ = 9.0 M, $C_{H2O,0}$ = 31.2 M
2	$C_{NM,0}$ = 1.4 M, $C_{HCl,0}$ = 1.5 M, $C_{H2O,0}$ = 46.8 M
3	$C_{NM,0}$ = 2.1 M, $C_{HCl,0}$ = 1.5 M, $C_{H2O,0}$ = 43.0 M
4	$C_{NM,0}$ = 2.8 M, $C_{HCl,0}$ = 3.4 M, $C_{H2O,0}$ = 37.3 M
5	$C_{NM,0}$ = 3.8 M, $C_{HCl,0}$ = 5.6 M, $C_{H2O,0}$ = 29.9 M
6	$C_{NM,0}$ = 1.4 M, $C_{H2O,0}$ = 44.5 M, $C_{HCl,0}$ varied from 1.0 M to 8.2 M
7	$C_{NM,0}$ = 3.0 M, $C_{HCl,0}$ = 7.5 M, $C_{H2O,0}$ = 28.5 M
8	$C_{NM,0}$ = 3.0 M, $C_{HCl,0}$ = 7.5 M, $C_{H2O,0}$ = 36.6 M
9	$C_{NM,0}$ = 1.4 M, $C_{HCl,0}$ = 8.2 M, $C_{H2O,0}$ = 31.2 M
10	$C_{NM,0}$ = 1.4 M, $C_{HCl,0}$ = 8.2 M, $C_{H2O,0}$ = 39.1 M
11	$C_{NM,0}$ = 1.4 M, $C_{HCl,0}$ = 2.5 M, $C_{H2O,0}$ = 45.6 M
12	$C_{NM,0}$ = 1.4 M, $C_{HCl,0}$ = 3.4 M, $C_{H2O,0}$ = 44.6 M
13	$C_{NM,0}$ = 1.4 M, $C_{HCl,0}$ = 4.3 M, $C_{H2O,0}$ = 43.3 M
14	$C_{NM,0}$ = 2.1 M, $C_{HCl,0}$ = 1.5 M, $C_{H2O,0}$ = 43.0 M
15	$C_{NM,0}$ = 2.1 M, $C_{HCl,0}$ = 3.2 M, $C_{H2O,0}$ = 40.9 M
16	$C_{NM,0}$ = 1.4 M, $C_{HCl,0}$ = 1.0 M, $C_{H2O,0}$ = 47.4 M
17	$C_{NM,0}$ = 1.4 M, $C_{HCl,0}$ = 6.8 M, $C_{H2O,0}$ = 40.6 M
18	$C_{NM,0}$ = 3.8 M, $C_{HCl,0}$ = 8.3 M, $C_{H2O,0}$ = 30.6 M
19	$C_{NM,0}$ = 0.7 M, $C_{HCl,0}$ = 3.1 M, $C_{H2O,0}$ = 48.3 M
20	$C_{NM,0}$ = 1.4 M, $C_{HCl,0}$= 3.0 M, $C_{H2O,0}$ = 40.6 M

[a] $C_{NM,0}$, $C_{HCl,0}$, $C_{H2O,0}$ represent the initial concentration of NM, HCl and water respectively. M is equivalent to mol/L

Analysis method

Gas chromatography (GC) analysis

NM in reaction mixture was extracted with toluene. The phase mass ratio between toluene and reaction mixture was 10. With the salting-out effect, anhydrous sodium sulfate (20 wt % to reaction mixture) was added into the mixture before adding the extractant for more sufficient extraction of NM.

Internal standard method was used to quantify the content of NM in the extract. *N*-pentanol was chosen as internal standard substance. Samples of known concentrations were tested to get the extraction rate. The results were listed in Table. S2. The average extraction rate of 0.96 was selected to determine the mass of NM in the mixture for the following kinetics experiments. Detailed analysis conditions were as following:

Polar capillary column: DB-WAXETR, 30 m × 0.250 mm i.d.

Nitrogen as the carrier gas, 1 ul sample size with 10:1 split ratio.

Injection temperature: 210 °C.

FID detector temperature: 220 °C.

Temperature programmed method: initial temperature 50 °C remaining for 5 min, then elevating the temperature to 80 °C by 10 °C /min remaining for 5 min, finally increasing the temperature by 30 °C /min to 200 °C remaining for 5 min.

Table S2 Tests to determine the extraction rate

Test [a]	Extraction rate [b]
1	0.943
2	0.977
3	0.955
4	0.965

[a] Mass fraction of NM in the mixture of test 1-4 was 1 wt %, 2 wt %, 3 wt %, 4 wt %, respectively. [b] Extraction rate is defined as $\frac{Mass\ of\ NM\ in\ extract}{Mass\ of\ NM\ in\ mixture}$

UV-vis spectrophotometry analysis

The UV-vis spectrum of NM was shown in Fig. S1. The two absorption peaks of NM centered at 226 and 268 nm, respectively. The existence of HCl, HCOOH and $NH_2OH \cdot HCl$ didn't interfere with the UV absorption of NM. The absorbance at 226 nm was too sensitive to the concentration of NM. Therefore, we chose the absorbance at 268 nm to quantify the content of NM. A series of concentrations of NM aqueous solution were prepared and then the absorbance was determined. The standard curve was plotted (Fig. S2) and used to determine the content of NM.

Comparing the analysis results between GC and UV-vis spectrophotometry

The reaction mixture was analyzed with this two methods to obtain the conversion of NM. The analysis results was compared and detailed in Table. S3. Results got by two methods were close to each other. The relative error may result from the varied extraction rate with the different composition of the mixture. Because of simple sample preparation and time-saving, UV-vis spectrophotometry was chose as the analysis method for all kinetics experiments.

Table S3 The conversion of NM obtained by GC and UV-vis spectrophotometry analysis

Entry [a]	Reaction time (min)	$X_{NM, GC}$ (%) [b]	$X_{NM, UV}$ (%) [b]	Relative error (%) [c]

1	40	20.4	21.4	4.6
	50	24.4	25.0	2.4
	60	26.8	27.3	1.8
2	40	11.4	11.7	2.6
	50	14.9	15.4	3.2
	60	16.3	16.4	0.6

[a] pre-experimental conditions: $C_{NM,0}$ = 1.4 M, $C_{HCl,0}$ = 2.7 M, $C_{H2O,0}$ = 45.2 M, T = 110 ℃ and 100 ℃ for entry 1 and 2, respectively. [b] $X_{NM,\ GC}$ and $X_{NM,\ UV}$ represent the conversion of NM determined by GC and UV-vis spectrophotometry. [c] Relative error is defined as

$$\frac{|x_{NM,\ GC}-x_{NM,\ UV}|}{x_{NM,\ UV}}$$

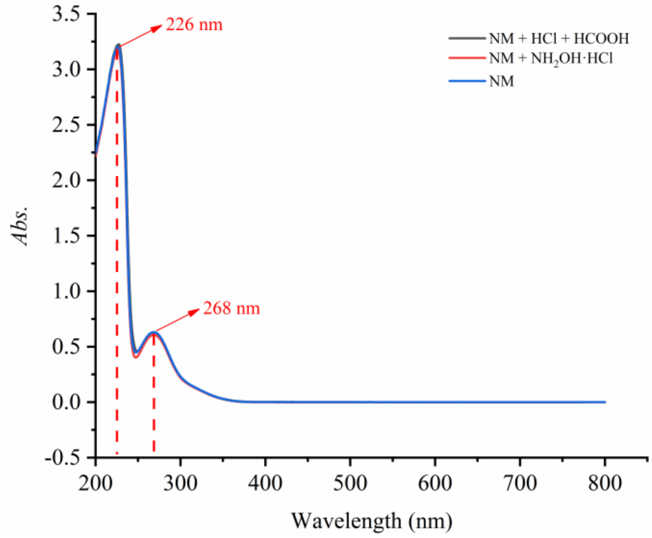

Fig. S1 The UV-vis spectrum of NM. The presence of HCl, HCOOH and $NH_2OH·HCl$ has no interference with the UV absorption of NM.

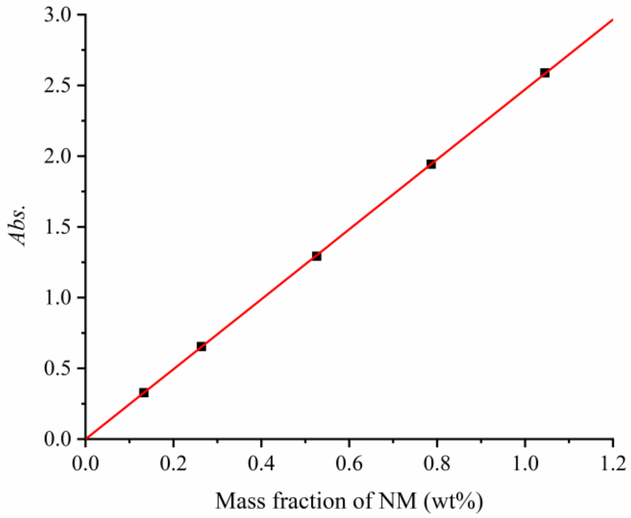

Fig. S2 Standard curve for determining the content of NM. The expression was Abs. = 2.47 × Mass fraction with R-square = 0.9999.

Determining the yield of $NH_2OH·HCl$

The product solution was diluted with three volumes of ethanol in a glass bottle. The crystal of $NH_2OH·HCl$ was obtained by reduced pressure distillation of the diluent at 60 °C. The crystal was dissolved again in the ethanol. Repeat the above operation for three times and ensure that all the unreacted regents were removed. The weight of the product was obtained by subtracting the bottle weight (w_b) from the total weight (w_t) of the bottle and product. The yield of product was calculated according to the following equation, in which $Y_{NH_2OH·HCl}$ represents the yield of $NH_2OH·HCl$ (%), $M_{NH2OH·HCl}$ is the molecular weight of $NH_2OH·HCl$ (g/mol), n_{NM} is the moles of NM in reaction mixture (mol).

$$Y_{\mathrm{NH_2OH \bullet HCl}} = \frac{(w_{\mathrm{t}} - w_{\mathrm{b}})}{M_{\mathrm{NH_2OH \bullet HCl}} \times n_{\mathrm{NM}}}$$

The integral form of second-order model

Differential form of the second-order model:

$$\frac{dX_{\mathrm{NM}}}{dt} = k_2\left(1 - X_{\mathrm{NM}}\right)\left(C_{\mathrm{HCl,\,0}} - C_{\mathrm{NM,0}}X_{\mathrm{NM}}\right) \tag{S1}$$

Modifying the eqn (S1):

$$\frac{1}{C_{\mathrm{HCl,0}} - C_{\mathrm{NM,0}}}\left(\frac{1}{1\text{-}X_{\mathrm{NM}}} - \frac{1}{C_{\mathrm{HCl,0}} - C_{\mathrm{NM,0}}X_{\mathrm{NM}}}\right)\frac{dX_{\mathrm{NM}}}{dt} = k_2 dt \tag{S2}$$

Integrating the eqn (S2):

$$\frac{-1}{\left(C_{\mathrm{HCl,\,0}} - C_{\mathrm{NM,0}}\right)}\ln\left(\frac{1 - X_{\mathrm{NM}}}{C_{\mathrm{HCl,0}} - C_{\mathrm{NM,0}}X_{\mathrm{NM}}}\right) = k_2 t + \frac{1}{\left(C_{\mathrm{HCl,\,0}} - C_{\mathrm{NM,0}}\right)}\ln C_{\mathrm{HCl,0}} \tag{S3}$$

Plotting the term $\frac{-1}{\left(C_{\mathrm{HCl,\,0}} - C_{\mathrm{NM,0}}\right)}\ln\left(\frac{1 - X_{\mathrm{NM}}}{C_{\mathrm{HCl,0}} - C_{\mathrm{NM,0}}X_{\mathrm{NM}}}\right)$ vs *t*, we can get the second-order rate constant k_2.

Apparent activation energy

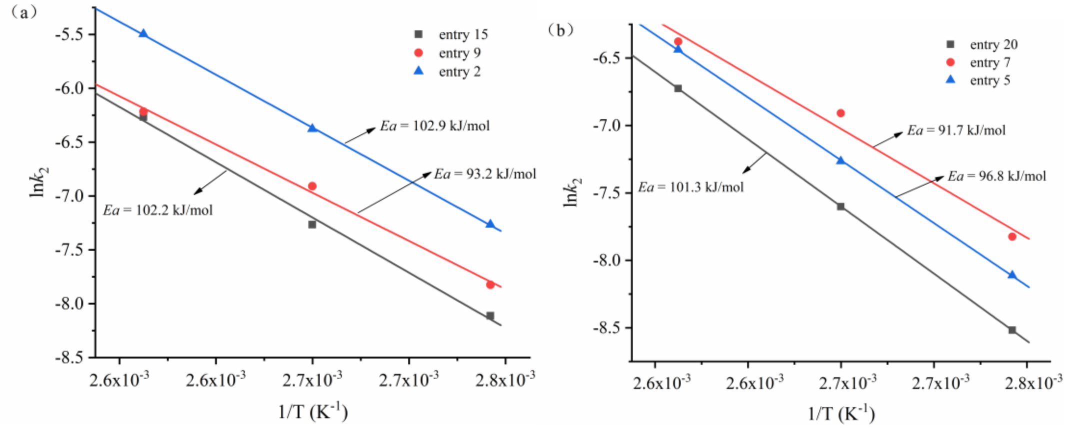

Fig. S3 The apparent activation energy (a) in diluted acid and (b) concentrated acid.