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Kinetic study on methyl nitrite synthesis from methanol and dinitrogen trixiode

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ABSTRACT

The kinetics of synthesizing methyl nitrite via the gas–liquid reaction of N_2O_3 with methanol was studied in a double-stirred cell reactor with a plane, horizontal gas–liquid interface, in the temperature range of 278–298 K. Since N_2O_3 is stable only below 0 °C, a mixture of NO and NO_2 with the ratio of 1:1 behaves chemically like N_2O_3 and replaces it. The Henry's constants and diffusion coefficients of NO and NO_2 in the liquid phase were estimated, and it was found that the generating rate of methyl nitrite was only affected by the partial pressure of NO in the gas phase. The reaction between N_2O_3 and methanol was fast pseudo-first order, and a kinetic equation was obtained as follows:

$$R_{MN} = 2\frac{P_{NO}}{H_{NO}}C^0\sqrt{D_{NO} \times 6.546 \times 10^9 \exp\left(-\frac{57,416}{RT}\right) \times C^0}$$

1. Introduction

Methyl nitrite (MN) has been found useful in a variety of areas including additives to motor fuels, stabilizer for vinyl compounds such as spasmolytic agents, reagents for diazotization and for chemical synthesis. Now, the most important purpose of MN is to produce dimethyl oxalate (DMO), and then DMO is hydrogenated to produce ethylene glycol (EG).

The means of preparing EG from syngas is of considerable industrial importance and has good potential outlook, in particular, to solve the energy problem in some areas being affluent in coal, when the price of petroleum is high. Regenerating MN is very important in this technic, but very little investigation was reported. The reaction distillation was applied to regenerate MN [1,2], whereas, the kinetic data were very poor. Chen [3] has investigated this gas–liquid reaction in a laboratory-size packed tower and relevant kinetic data have been reported. However, these macrokinetic data cannot be used in industrial scaling-up for a great deal of differences between industrial column and laboratory-size.

Accordingly, a double-stirred reactor was introduced to research the kinetics of synthesizing MN from methanol and N_2O_3, which is typically used to investigate the gas–liquid reaction. Although N_2O_3 is stable only below 0 °C, a mixture of NO and NO_2 with the ratio of 1:1 behaves chemically like N_2O_3 [4], and is substitutes it.

2. Theory

2.1. The reaction theory of synthesizing MN

Some patents [1,2] reviewed the main reactions of N_2O_3 with methanol:

$$CH_3OH(l) + N_2O_3(g) \rightarrow CH_3ONO(g) + HONO(l) \quad (1)$$

$$CH_3OH(l) + HONO(l) \rightarrow CH_3ONO(g) + H_2O(l) \quad (2)$$

Overall reaction:

$$2CH_3OH(l) + N_2O_3(g) \xrightarrow{k} 2CH_3ONO(g) + H_2O(l) \quad (3)$$

Since N_2O_3 was replaced by the mixture of NO and NO_2 with the ratio of 1:1, the following side reactions may also take place simultaneously:

$$H_2O(l) + N_2O_3(g) \rightarrow 2HONO(l) \quad (4)$$

$$2NO_2(g) \leftrightarrows N_2O_4(g) \quad (5)$$

$$N_2O_4(g) + CH_3OH(g) \rightarrow CH_3ONO(g) + HNO_3(l) \quad (6)$$

$$H_2O(l) + N_2O_4(g) \rightarrow HONO(l) + HNO_3(l) \quad (7)$$

Excessive methanol can eliminate the generation of nitrous acid, because the reaction between methanol and HONO (Eq. (2)) is almost instantaneous [5]. The reactions (Eqs. (5)–(7)) reveal that N_2O_4 in gas phase accounts for the by-product of nitric acid formation. Though there is an equilibrium between NO_2 and N_2O_4 (Eq.

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Nomenclature

$C^*_{N_2O_3}$	concentration of dissolved N_2O_3 at interface, in equilibrium with gas at interface (kmol/m^3)
$C^0_{N_2O_3}$	concentration of N_2O_3 in bulk liquid (kmol/m^3)
$C^0_{CH_3OH}$	concentration of CH_3OH in bulk liquid (kmol/m^3)
C^0	concentration of absolute methanol (kmol/m^3)
D_{CH_3OH}	diffusion coefficient of CH_3OH in liquid phase (m^2/s)
$D_{N_2O_3}$	diffusion coefficient of N_2O_3 in liquid phase (m^2/s)
D_{NO}	diffusion coefficient of NO in liquid phase (m^2/s)
E^0	activation energy (J/mol)
E	enhancement factor
E_i	enhancement factor when reaction is instantaneous
$H_{N_2O_3}$	Henry's constant of N_2O_3 in methanol (Pa)
H_{NO}	Henry's constant of NO (Pa)
Ha	$\sqrt{D_{N_2O_3}kC^0_{CH_3OH}/K_L}$, Hatta number
k	reaction rate constant in Eq. (3) (m^3/(kmol s))
K_L	liquid-side mass-transfer coefficient (m/s)
k_0	pre-exponential factor (m^3/(kmol s))
n_L	agitation speed in liquid (rpm)
n_G	agitation speed in gas (rpm)
n_i	mole quantities of component i in the constant ring of the gas chromatograph (mol)
P_i	partial pressure of component i in the reactor (Pa)
P_0	total pressure of the vent (MPa)
$P_{N_2O_3}$	partial pressure of N_2O_3 in gas phase (Pa)
P_r	pressure of the double-stirred reactor ($\times 10^5$ Pa)
P_{NO}	partial pressure of NO in gas phase (Pa)
R	consuming rate of N_2O_3 (kmol/(m^2 s))
R_i	mole rate of component i in the vent (mol/s)
R_g	gross mole rate of component in the vent (mol/s)
R_{MN}	synthesizing rate of MN by N_2O_3 and methanol (kmol/(m^2 s))
R^0_{MN}	gross rate of MN in the vent (kmol/(m^2 s))
R_{acid}	generating rate of nitric acid (kmol/(m^2 s))
T	temperature (K)
T^0	temperature of the vent (K)
v'	total rate of gas from the reactor(m^3/s)
v_c	volume of constant ring of the gas chromatograph (m^3)
x	distance beneath liquid surface (m)
δ	thickness of diffusion film (m)

(5)), the equilibrium is shifted almost all the way toward NO_2 at higher temperature [4] (100 °C). Accordingly, the temperature of feed must be higher than 100 °C and lower than 150 °C for the dissociation of NO_2 [4]. If not, N_2O_4 will exist in the feed. Nevertheless, the reactor's temperature is generally below 100 °C, the reactions (Eqs. (5)–(7)) will take place in the double-stirred reactor. Thus, the rate of MN (R^0_{MN}) detected in the vent is the total generating rate of MN in this system. The generating rate of MN and nitric acid (R_{acid}) by side reactions is equal so that the producing rate of MN (R_{MN}) by main reaction (Eq. (3)) can be expressed as:

$$R_{MN} = R^0_{MN} - R_{acide} \tag{8}$$

The limited step for synthesizing MN is the reaction between methanol and N_2O_3 (Eq. (1)), because of the instantaneous reaction of methanol with nitrous acid (Eq. (2)). Therefore, the reaction of synthesizing MN is irreversible second order. Using two-film model theory to calculate the material balance of components, the relevant equations were formed as follows [6]:

$$D_{N_2O_3}\frac{d^2C_{N_2O_3}}{dx^2} - kC_{N_2O_3}C_{CH_3OH} = 0 \tag{9}$$

$$D_{CH_3OH}\frac{d^2C_{CH_3OH}}{dx^2} - 2kC_{N_2O_3}C_{CH_3OH} = 0 \tag{10}$$

With

$$\begin{aligned} C_{N_2O_3} &= C^*_{N_2O_3}, & \chi &= 0 \\ C_{N_2O_3} &= C^0_{N_2O_3}, & \chi &= \delta \\ C_{CH_3OH} &= C^0_{CH_3OH}, & \chi &= \delta \\ \frac{dC_{CH_3OH}}{dx} &= 0, & \chi &= 0 \end{aligned} \tag{11}$$

An analytical solution of the above equations is not available, but an approximate set of solutions for the case $C^0_{N_2O_3} = 0$ has been computed by van Krevelen and Hoftijizer, and the enhancement factor was expressed as:

$$E = \frac{\sqrt{Ha^2((E_i - E)/(E_i - 1))}}{\tanh\sqrt{Ha^2((E_i - E)/(E_i - 1))}} \tag{12}$$

where

$$E = \frac{R}{K_L C^*_{N_2O_3}}; \qquad E_i = \left(1 + \frac{D_{CH_3OH}C^0_{CH_3OH}}{2D_{N_2O_3}C^*_{N_2O_3}}\right)$$

There were two methods for simplifying the above enhancement factor:

$$\text{if } Ha > 10E_i \tag{13}$$

It means that the gas–liquid reaction is instantaneous, and the enhancement is expressed as:

$$E = E_i \tag{14}$$

On the other hand, if

$$Ha < \frac{1}{2}E_i \tag{15}$$

The gas–liquid reaction is pseudo-first order which means that the reaction is sufficiently slow or the physical mass-transfer coefficient is large enough so that the concentration of reactant is maintained virtually undepleted with its bulk concentration $C^0_{CH_3OH}$ holding up to the surface. In addition:

$$Ha > 3 \tag{16}$$

If the above requirements (Eqs. (15) and (16)) are satisfied, the gas–liquid reaction is fast pseudo-first order and the enhancement is shown as:

$$E = Ha \tag{17}$$

2.2. Planning of preparing the mixture of NO and NO_2 with the ratio of 1:1

The mixture of NO and NO_2 with the ratio of 1:1 was prepared in an isothermal tubular reactor with the mixture of 80% NO–20% O_2 charged inside. The process of nitrogen oxide oxidization was simulated in an isothermal tubular reactor with the temperature of 100 °C and atmospheric pressure (the kinetic data from literature [4]). The relationship between the components' partial pressure and residence time is plotted in Fig. 1. Fig. 1 shows that the partial pressure of NO was equal to NO_2 when the residence time went beyond 18 s and no oxygen existed.

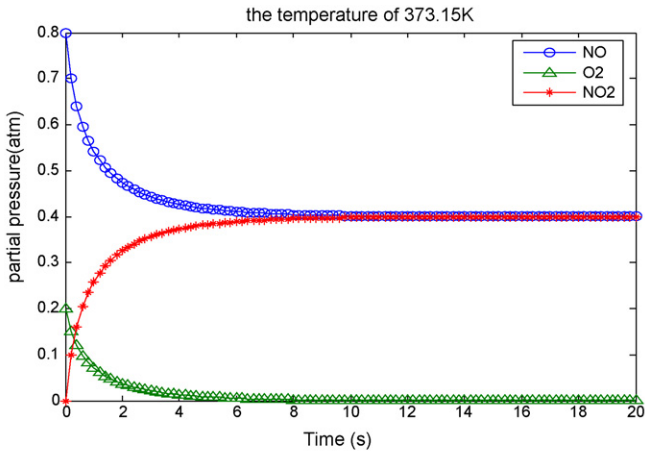

Fig. 1. The simulated result of nitrogen monoxide oxidization by Matlab.

3. Experimental

3.1. Materials

Absolute methanol (AR), used in all of the experiments, was purchased from Sinopharm. A nitrogen monoxide cylinder with a given purity of 99.2% was purchased from DGC. Nitrogen cylinders and oxygen with a purity of 99.99% were purchased from Wugang. Caustic soda (AR) was purchased from Lingfeng.

3.2. Experimental set-up

A schematic diagram of the experiment apparatus is shown in Fig. 2. NO and O_2 from the cylinders with the ratio of 4:1 were charged into an isothermal tubular reactor with the temperature of 100 °C and atmospheric pressure, which was 500 ml in volume and 4 cm in internal diameter. The isothermal tubular reactor had an oil jacket to control temperature, whose temperature was managed by a thermostat. The deviation of the oil temperature was within 0.1 °C. The tubes between the isothermal reactor and the double-stirred reactor were adiabatic and made of Teflon. The reaction of methanol with the mixture of NO and NO_2 with the ratio of 1:1 was carried out in the double-stirred reactor. The details have been reported by Mao [7]. Therefore, only a few essentials were repeated here.

Most of the experiments were performed with a liquid stirring speed (n_L) of 200 rpm and a gas stirring speed (n_G) of 300 rpm (excluding specification).

3.3. Analytical method

The concentrations of NO and MN, O_2 in the gas phase were measured by two gas chromatographs (GC7890T, Techcomp), one was equipped with 13X molecular sieve packed column with 5 m in length for analyzing NO and O_2, and the other one was equipped with GDX101 carbon molecular sieve packed column with 3 m in length for analyzing MN. The molar quantities acid of the liquid phase in the double-stirred reactor was analyzed by neutralization titration, taking phenolphthalein as indicator and a concentration of 0.05 mol caustic lye of soda as titrant. The error in all experimental measurements was found to be less than 3%.

3.4. Experimental procedure

A series of experiments were conducted at different temperatures (278–298 K). In each experiment, the double-stirred reactor was charged with 200 ml of absolute methanol from the liquid reservoir (excluding specification). It was then purged with nitrogen to weep the double-stirred reactor to ensure an inert atmosphere. The reactor attained the desired temperature, and then the mixture of NO and NO_2 with the ratio of 1:1 from the isothermal tubular reactor was charged inside. Meanwhile, the flow of nitrogen was adjusted to desired quantity. After about 75 min, the gas phase and liquid were analyzed, as the gas–liquid reaction attained steady state. The sampling time interval was 15 min and the amount of each liquid sample was only 1 ml. Owing to the volatilization of absolute methanol and sampling, a small quantity of absolute methanol was charged inside the double-stirred reactor to keep the volume of liquid constant during the experiments.

3.5. Data analysis

The gas–liquid reaction in the double-stirred reactor was perfect mixing. Therefore, the efflux components' concentration of the reactor was in the same with that in the reactor. The mole rate of component i in the vent can be obtained by gas chromatograph (v_c, n_i) and soap film meter (v'):

$$R_i = \frac{v' n_i}{v_c} \tag{18}$$

The total mole rate in the vent can be calculated by ideal gas equation, for the outflow pressure was not very high:

$$R_g = \frac{v' P_0}{RT^0} \tag{19}$$

The partial pressure of component i can be expressed as:

$$P_i = p_r \frac{R_i}{R_g} \tag{20}$$

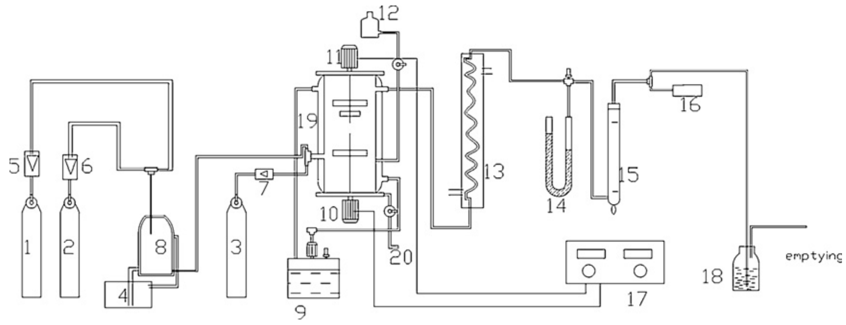

Fig. 2. Schematic diagram of the experimental apparatus. (1) NO cylinder; (2) O_2 cylinder; (3) N_2 cylinder; (4) oil bath; (5–7) mass flow meter; (8) isothermal tubular reactor; (9) water bath; (10 and 11) driving motor; (12) liquid reservoir; (13) condenser; (14) pressure gauge; (15) soap film meter; (16) gas chromatograph; (17) stirring speed controller; (18) tail gas absorber; (19) stirred cell; (20) sample connection.

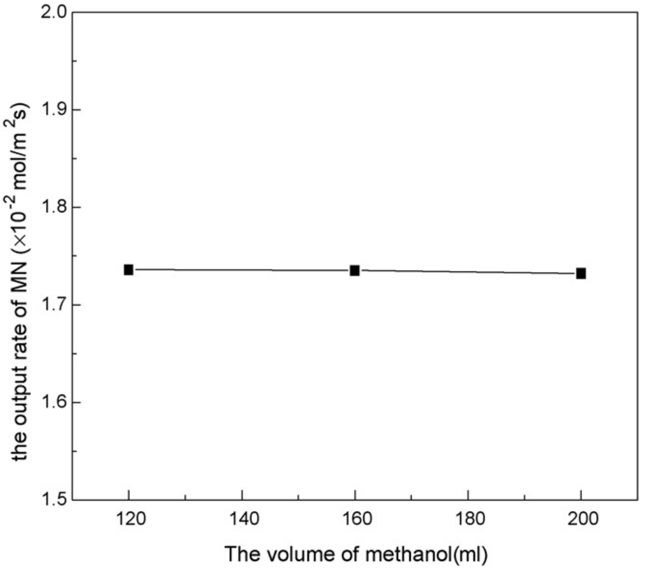

Fig. 3. Effect of the volume of absolute methanol on generating MN rate. Gas–liquid interfacial area = 28.6 cm^2, NO inlet rate = 80 ml min^{-1} (NTP), O_2 in let rate = 20 ml min^{-1} (NTP), N_2 in let rate = 100 ml min^{-1} (NTP) and water bath temperature = 25 °C.

4. Results and discussion

4.1. Ascertaining the type of reaction of N_2O_3 with methanol

In order to ascertain the gas–liquid reaction's type, a series of experiments were conducted. Fig. 3 shows that the generating rate of MN was not influenced by the volume of absolute methanol. It can be concluded that the reaction between N_2O_3 and methanol was quick or instantaneous [8].

Fig. 4 exposes that the synthesizing rate of MN was not affected by the liquid stirring speed, which means that the kinetic rate was independent of the liquid-side mass-transfer coefficient K_L. Consequently, it can be conducted that the reaction between N_2O_3 and absolute methanol was fast pseudo-first order [6,9,10]. Because the enhancement factor is equal to Hatta number (Eq. (17)) in the fast pseudo-first-order reaction regime, and the liquid-side mass-transfer coefficient was removed in the reaction rate's expression.

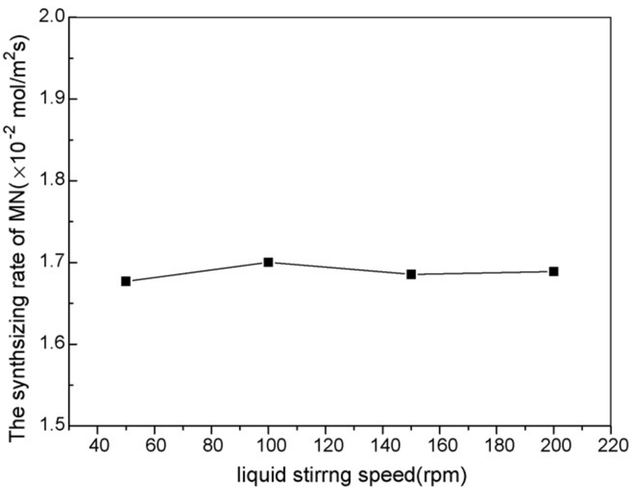

Fig. 4. Effect of liquid stirring speed on generating MN rate. Gas–liquid interfacial area = 28.6 cm^2, NO inlet rate = 80 ml min^{-1} (NTP), O_2 in let rate = 20 ml min^{-1} (NTP), N_2 in let rate = 100 ml min^{-1} (NTP) and water bath temperature = 25 °C.

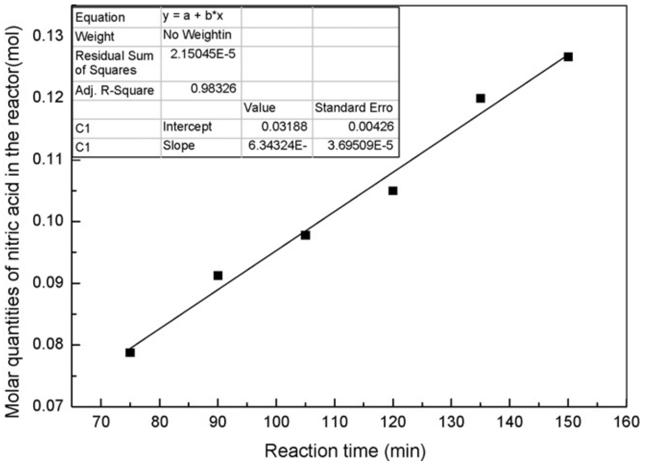

Fig. 5. Generating rate of nitric acid. Gas–liquid interfacial area = 28.6 cm^2, NO in let rate = 88 ml min^{-1} (NTP), O_2 in let rate = 22 ml min^{-1} (NTP), N_2 in let rate = 90 ml min^{-1} (NTP) and water bath temperature = 10 °C.

The fast pseudo-first-order reaction rate was expressed as [6]:

$$R = 2C^*_{N_2O_3}\sqrt{D_{N_2O_3}kC^0} \tag{21}$$

4.2. The generating rate of nitric acid

Aforesaid, the rate of MN (R^0_{MN}) in the vent must knock off the generating rate of nitric acid (R_{acid}) to get R_{MN}. The generating rate of nitric acid was obtained by plotting nitric acid's molar quantities in double-stirred reactor vs time after the gas–liquid reaction reaching steady state. One of fitting results was displayed in Fig. 5.

4.3. Kinetic equation

Since the concentration of N_2O_3 in the bulk liquid and water was very low, the liquid phase can be taken for methanol, and the concentration was constant. The fast pseudo-first-order reaction rate (Eq. (21)) was displayed as:

$$R_{MN} = 2\frac{P_{N_2O_3}}{H_{N_2O_3}}C^0\sqrt{\{D_{N_2O_3}kC^0\}} \tag{22}$$

As afore mentioned, N_2O_3 was replaced by the mixture of NO and NO_2 with the ratio of 1:1 in the reactor, therefore, considering that NO and NO_2 reacted simultaneously with methanol, not considering merely N_2O_3 . Using limited step's thoughtway, the Henry's constants and diffusion coefficients of NO and NO_2 in the liquid phase were estimated to find out the pro-dominated gas in this reaction. The diffusion's constants of nitrogen oxide and nitrogen dioxide were estimated by the equation of Wilke and Chang [6].

The estimated diffusion's constant is shown in Table 1, the values of diffusion coefficient of NO were as much as nitrogen dioxides at different temperatures. Therefore, the quadratic root of the both gas diffusion constants can be taken for equality.

There are some means to estimate Henry's constant, for instance, the means of Pierotti [12], the infinite dilution activity

Table 1
Diffusion constants estimated by Wilke and Change's equation.

Temperature (K)	D_{NO} $\times 10^5$ (cm^2/s)	D_{NO_2} $\times 10^5$ (cm^2/s)
278	3.1689	3.7993
283	3.5023	4.1991
288	3.8383	4.6026
293	4.2303	5.0720
298	4.6098	5.5270

The relevant parameters' values came from literatures [6,11].

Table 2
The Henry's constants of NO and NO_2 in methanol solvent at different temperatures.

Temperature (K)	$H_{NO} \times 10^{-7}$ (cm^2/s)	$H_{NO_2} \times 10^{-6}$ (cm^2/s)
278	1.8970	6.3937
283	2.0106	6.9006
288	2.1270	7.4285
293	2.2462	7.9773
298	2.3681	8.5467

The relevant parameters' values came from literatures [17–20].

coefficient means [13], the principle of corresponding state means [14], the molecular thermodynamics means [15,16]. In this work, the Henry's constants of NO and NO_2 in methanol were estimated by the molecular thermodynamic means. It can be estimated with more accuracy in polar solvents by the molecular thermodynamics. The Henry's constants of NO and NO_2 in methanol solvent at different temperatures are displayed in Table 2.

Table 2 reveals that the Henry's constants of nitrogen monoxide's values in methanol solvent are three times of nitrogen dioxide's at different temperatures, which means that the concentration of NO in the liquid phase was much less than nitrogen dioxides' and controlled the reaction rate while NO and NO_2 were changed into the double-stirred reactor with the same partial pressure. Consequently, it can be concluded that the parameters of N_2O_3 in the kinetic equation (Eq. (22)) can be superseded by the nitrogen monoxides', and the nitrogen dioxide's concentration did not need to be analyzed. It would reduce the difficulty in analyzing the concentration of NO_2 in the gas phase. Because, the peaks of NO_2, N_2 and N_2O_4 were overlapped mutually in gas chromatogram. Accordingly, the kinetic equation (Eq. (22)) can be represented as:

$$R_{MN} = 2\frac{P_{NO}}{H_{NO}} C^0 \sqrt{\{D_{NO} k C^0\}} \tag{23}$$

The synthesizing rate of MN by N_2O_3 and methanol and the values of rate constants at various temperatures calculated by Eq. (23) are displayed in Table 3.

Table 3
Rate constant of synthesizing MN at different temperatures.

Temperature (K)	P_{NO} (kPa)	$R_{MN} \times 10^5$ (mol/s)	k (m^3/(kmol s))
278	13.25	0.96742	0.1107
	15.43	1.13875	0.1131
	17.43	1.18345	0.0958
	22.81	1.51980	0.0913
	25.68	1.74364	0.0958
283	11.09	0.93304	0.1548
	12.58	1.07260	0.1590
	13.35	1.07915	0.1430
	13.98	1.17372	0.1542
	17.21	1.46622	0.1587
288	5.30	0.60610	0.3025
	5.73	0.66610	0.3126
	7.59	0.85620	0.2944
	9.48	1.05530	0.2866
	11.30	1.28970	0.3013
293	5.89	0.79523	0.4418
	6.25	0.83330	0.4308
	10.92	1.40530	0.4014
	13.05	1.65306	0.3889
	15.67	1.98733	0.3898
298	4.54	0.63042	0.4935
	8.44	1.20007	0.5175
	8.66	1.20482	0.4954
	10.92	1.50474	0.4860
	11.40	1.55934	0.4789

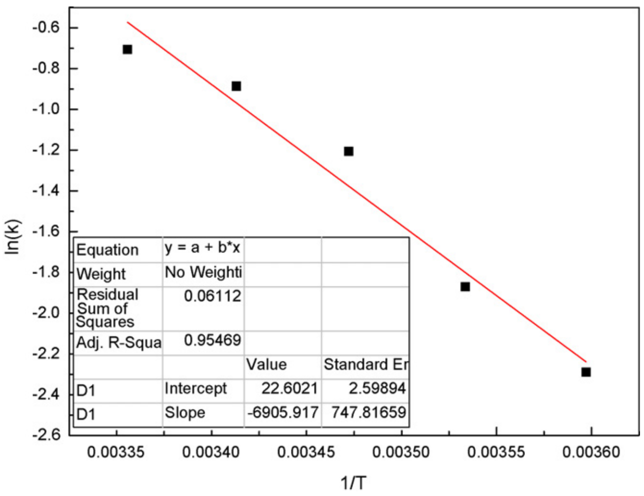

Fig. 6. The plot of ln k vs. $1/T$.

The rate constant can be expressed by Arrhenius' law [21]:

$$k = k_0 \exp\left(-\frac{E_0}{RT}\right) \tag{24}$$

Mathematical manipulation of above-mentioned expression is as follows:

$$\ln k = -\frac{E^0}{RT} + \ln k^0 \tag{25}$$

Actually, the gas–liquid reaction was approximate steady state. Therefore, there were fluctuations in above calculated rate constants at the same temperature. The values of pre-exponential factor and activation energy could be gained by plotting the average values of rate constants' natural logarithm at different temperatures vs. $1/T$. The value of slope was $-(E^0/R)$, and the value of intercept was $\ln k_0$. Fig. 6 shows the results of fitting. Finally, the kinetic equation can be represented as:

$$R_{MN} = 2\frac{P_{NO}}{H_{NO}} C^0 \sqrt{D_{NO} \times 6.546 \times 10^9 \exp\left(-\frac{57,416}{RT}\right) \times C^0} \tag{26}$$

5. Conclusions

The reaction of N_2O_3 with methanol was investigated in a double-stirred reactor while substituting N_2O_3 by the mixture of NO and NO_2 with the ratio of 1:1. The Henry's constants and diffusion coefficients of NO and NO_2 in absolute methanol were estimated, and the synthesizing rate of MN was merely influenced by the partial pressure of NO. It was ascertained that the reaction was fast pseudo-first order, and the kinetic equation was obtained as:

$$R_{MN} = 2\frac{P_{NO}}{H_{NO}} C^0 \sqrt{D_{NO} \times 6.546 \times 10^9 \exp\left(-\frac{57,416}{RT}\right) \times C^0} \tag{27}$$

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