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**Dan Wang**
College of Chemistry and Environmental Science, Hebei University, Key Laboratory of Analytical Science and Technology of Hebei Province, Baoding, Hebei, China

**Jinhuan Shan**
College of Chemistry and Environmental Science, Hebei University, Key Laboratory of Analytical Science and Technology of Hebei Province, Baoding, 071 002 Hebei, China

**Chaochao Chen**
College of Chemistry and Environmental Science, Hebei University, Key Laboratory of Analytical Science and Technology of Hebei Province, Baoding, 071 002 Hebei, China

**Correspondence**
**Jinhuan Shan**
College of Chemistry and Environmental Science, Hebei University, Key Laboratory of Analytical Science and Technology of Hebei Province, Baoding, 071 002 Hebei, China

# Oxidation of N-methyldiethanolamine and N, N-dimethyl ethanolamine by ditelluratoar – gentate (iii) in alkaline medium. A kinetic and mechanistic study

**Dan Wang, Jinhuan Shan and Chaochao Chen**

**Abstract**
In the temperature range of 288.2K-308.2K, the oxidation reaction of N-methyldi ethanlamine and N,N-dimethyl ethanolamine with ditelluratoargentate (III)(DTA) in alkaline medium has been studied spectrophotometrically. The reaction rate showed fraction order in N-methyldiethanolamine and N,N-dimethyl ethanolamine. With the increase of [reductant] and [$OH^-$], the rate constant $k_{obs}$ increased, but $k_{obs}$ decreased with the increase of [$TeO_4^{2-}$]. It was clear that the rate of N-methyldiethanolamine is higher than that of N,N-dimethyl ethanolamine. In addition, there is a negative salt effect on the reaction of N,N-dimethyl ethanolamine and N-methyldiethanolamine, the influence of salt effect is not very obvious. A plausible mechanism involving a slow reaction as the rate-controlled step is proposed and the rate equations derived from the mechanism can explain all the experimental results. Thus, the activation parameters at 298.2K were calculated.

**Keywords:** kinetics; ditelluratoargentate (III) (DTA); oxidation; N-methyldi ethanlamine; N,N-dimethyl ethanolamine

## 1. Introduction

Since the early 20th century, people have found the presence of the highest oxidation state of transition metals, many scholars, at home and abroad, made the subject of study in different extent. The highest oxidation state of transition metals often chelated with other polydentate ligand to form a new substance, that is transition metal chelate complexes, such as diperiodatoargentate (III) [1], ditelluratoargentate(III) [2], ditelluratocurprate(III) [3] and diperiodatonickelate (III) [4] .

The pure natural mineral silver ion has been recognised as one of the most safety, efficient, environmentally friendly antibacterial material by the international community. The valence of silver affects the bactericidal activity, the relative ability of sterilisation is as follows: Ag (Ⅲ)>Ag(Ⅱ)>Ag(Ⅰ)>Ag. The oxidation of some organic compounds and some in lower valence metals by Ag (Ⅲ) has been reported. Ag (Ⅲ) complexes as an efficient disinfectant, can be used to disinfect the pool water. Ag(Ⅲ) complexes as oxidant is very stable, so Ag(Ⅲ) can be used to oxidise some special biological molecules and drugs [5, 7], Ditelluratoargentate(Ⅲ) can used to oxidaise some organic that have simple radical [8] and some lower valence metals [9]. But the reaction system containing Ag (Ⅲ) as oxidant is complex, so if we want to understand the reaction, further research is needed.

N-methyldiethanolamine and N,N-dimethyl ethanolamine are important intermediates in organic synthesis. N-methyldiethanolamine is a new kind of selective desulphurization and decarburizing solvent, which has the advantages of high selectivity, low solvent consumption, significant energy saving and not easy to degrade. It is widely used in oil field gas and coal gas desulfurization and acid gas absorbing agent, acid alkali control agent, polyurethane foam catalyst. In recent years, the absorption of carbon dioxide in the flue gas has been gradually use it. In addition, semi-finished MDEA additives products can be used as a pesticide, emulsifier, fabric, antitumor drug intermediates and fiber additives, etc., at the same time, it is also a kind of paint drying agent. N,N-dimethyl ethanolamine as a catalyst can catalyze the reaction of aqueous epoxy groups, it also is the curing catalysts for polyurethane hot melt adhesives and catalysts for chelating reaction of resins with activated magnesia, in low temperature it can serve as curing accelerators for epoxy resins and polyurethane foams.

It is also used as neutralizing agent for water phase epoxy resin emulsion and waterborne polyurethane adhesive. In this paper, the kinetics mechanism of the oxidation of N-methyldi ethanolamine and N,N-dimethyl ethanolamine by ditelluratoargentate (III) (DTA) is reported.

## 2. Experimental

### 2.1 Materials

All chemicals used were of A.R. reagent grade. Doubly distilled water was prepared and used for all the solutions. The ditelluratoargentate(III) (DTA) crystals were synthesised via oxidising Ag (I) in alkaline medium and modified by the reported method earlier [10]. The product detected by UV/vis spectrum, and the absorption spectrum of ditelluratoargentate (III) complex showed an absorption maximum at 346 nm. KOH and $KNO_3$ were employed to regulate the alkalinity and ionic strength, thus creating a stable environment. The ditelluratoargentate (III) must be prepared again before using with doubly distilled water.

### 2.2 Kinetics measurements and apparatus

All kinetics measurements were performed under pseudo-first order conditions. The reaction contains two major substances, that is the ditelluratoargentate (III) serving as oxidant and the alcohol as reductant. In the oxidant ditelluratoargentate (III) added KOH, $K_2TeO_4$, $KNO_3$. The ionic strength was controlled by $KNO_3$ solution and the pH was maintained by KOH solution. The obtained absorption spectra of ditelluratoargentate (III) well agree with the reported ones [10]. The first peak is observed at 346 nm and the second at 265 nm for the ditelluratoargentate (III), respectively. The concentration of ditelluratoargentate (III) has an absorption peak at 346 nm. None of other species absorbed significantly at this wavelength. The kinetic measurements were carried on a SFM-2000 spectrophotometer (Bio-Logic, France), which had a cell holder kept at constant temperature (±0.1ºC) by circulating water from a thermostat (DC-2006, Baoding, China).

### 2.3 Product Analysis

When completely fading of the ditelluratoargentate (III) colour marked the reaction proceeded completely. The main product of oxidation was identified as the corresponding aldehyde by spot test [11].

## 3. Results and Discussion

Under the conditions of $[\text{reductant}]_0 >> [\text{Ag(III)}]_0$ , the plots of ln ($A_t$-$A_\infty$) versus time were straight lines, showing that the reaction to DTA is first order, where $A_t$ is the absorbance at time $t$ and $A_\infty$ at time infinite. The pseudo-first order rate constants $k_{obs}$ were calculated by the method of least squares ($r \geq 0.998$). The $k_{obs}$ values were calculated by an average method on the basis of at least three parallel experiments, and reproducibility was within ±5%.

### 3.1 Rate dependence on the [reductant]

In the temperature range of 283.2-308.2 K, the values of [DTA], $[OH^-]$, $[TeO_4^{2-}]$ and μ remain constant, the [N-methyldi ethanolamine] and [N,N-dimethyl ethanolamine] varied from 0.005 to 0.025 mol·l$^{-1}$ at different temperatures. Make the [reductant] as abscissa, [reductant]/$k_{obs}$ as ordinate. The diagram shows that $k_{obs}$ increased with the increase of reductant concentration and the plots of [reductant]/$k_{obs}$ versus [reductant] were straight lines with a positive intercept (Figs 1 and 2). In addition, a linear dependence was observed as fractional order term with reductant.

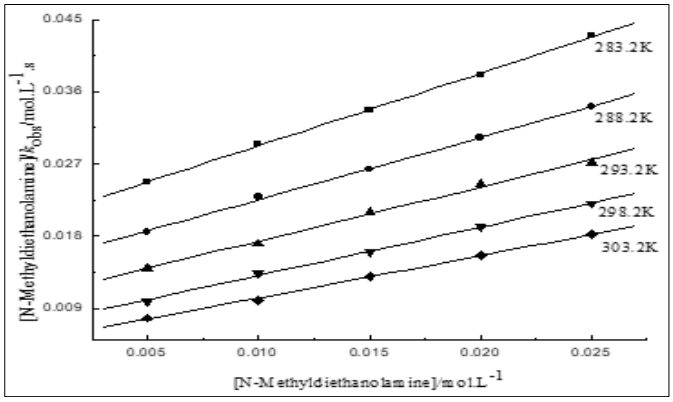


**Fig 1:** Plots of [N-methyldi ethanolamine]/$k_{obs}$ versus [N-methyldi ethanolamine].
[DTA] = 7.15 × 10$^{-4}$ mol·L$^{-1}$; $[TeO_4^{2-}]$ = 0.01 mol·L$^{-1}$; $[OH^-]$ = 1.00 × 10$^{-2}$ mol·L$^{-1}$; μ = 8.50 × 10$^{-2}$ mol·L$^{-1}$($r \geq 0.998$)

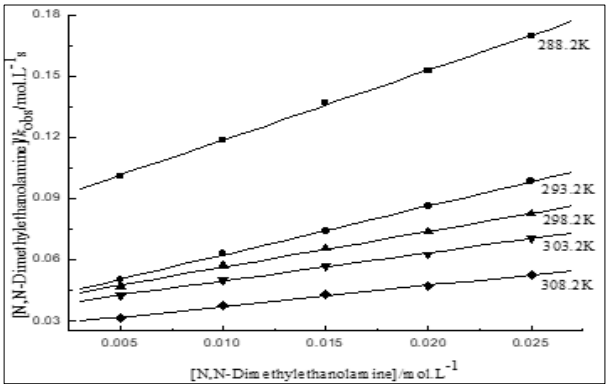


**Fig 2:** Plots of [N,N-dimethyl ethanolamine] /$k_{obs}$ versus [N,N-dimethyl ethanolamine].
[DTA] = 7.15 × 10$^{-4}$ mol·l$^{-1}$; $[TeO_4^{2-}]$ = 0.01mol·l$^{-1}$; $[OH^-]$ = 1.00 × 10$^{-2}$ mol·l$^{-1}$; μ = 8.50 × 10$^{-2}$ mol·l$^{-1}$ ($r \geq 0.998$)

### 3.2 Rate dependence on $[OH^-]$

At constant [DTA], [reductant], $[TeO_4^{2-}]$ and μ, $[OH^-]$ was varied in the range from 5 to 25 × 10$^{-3}$ moll·$^{-1}$. Make the 1/[OH] as abscissa, 1/$k_{obs}$ as ordinate. The plots of 1/$k_{obs}$ versus 1/$[OH^-]$ proved to be straight lines with a positive intercept, and $k_{obs}$ increased with the increased of $[OH^-]$ (Figs 3 and 4).

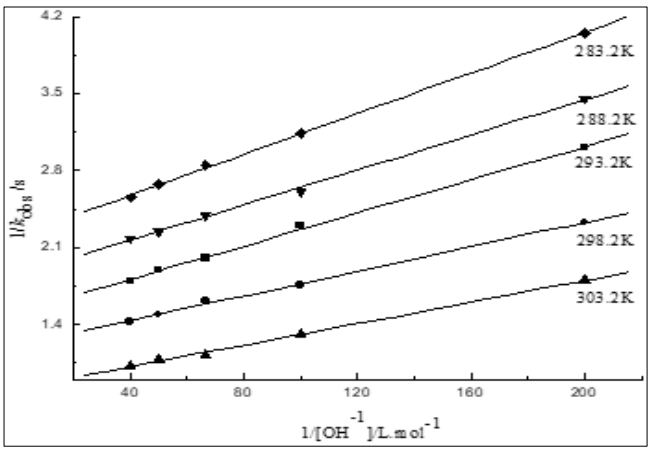


**Fig 3:** Plots of 1/$k_{obs}$ versus 1/ $[OH^-]$ at different temperatures
[DTA] = 7.15 × 10$^{-4}$ mol·l$^{-1}$; $[TeO_4^{2-}]$ = 0.01mol·l$^{-1}$; μ = 8.50 × 10$^{-2}$ mol·l$^{-1}$; [N-methyldiethanolamine] = 0.15 mol·l$^{-1}$($r \geq 0.998$)

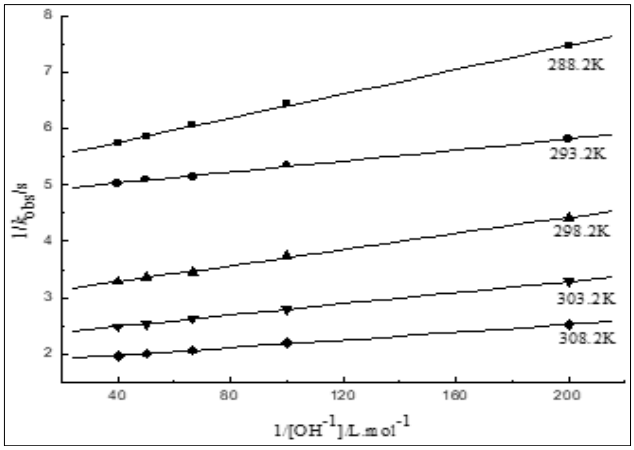


**Fig 4:** Plots of $1/k_{obs}$ versus $1/[OH^-]$ at different temperatures [DTA] = 7.15 × $10^{-4}$ mol·$l^{-1}$; [$TeO_4^{2-}$] =0.01mol·$l^{-1}$; μ = 8.50×$10^{-2}$ mol·$l^{-1}$; [N,N-dimethyl ethanolamine] = 0.15 mol·$l^{-1}$($r \geq 0.998$)

### 3.3 Rate dependence on [$TeO_4^{2-}$]

In the temperature range of 288.2-308.2K, ant constant concentrations of [DTA], [$OH^-$], [reductant] and μ, [$TeO_4^{2-}$] was varied in the range from 0.005 to 0.025 mol·$l^{-1}$. Make the [$TeO_4^{2-}$] as abscissa, $1/k_{obs}$ as ordinate. The plots of $1/k_{obs}$ versus [$TeO_4^{2-}$] were straight lines with positive intercept. The experimental results showed that $k_{obs}$ decreased with increase of [$TeO_4^{2-}$]. So there is an inverse relationship between $k_{obs}$ and [$TeO_4^{2-}$] (Figs 5 and 6).

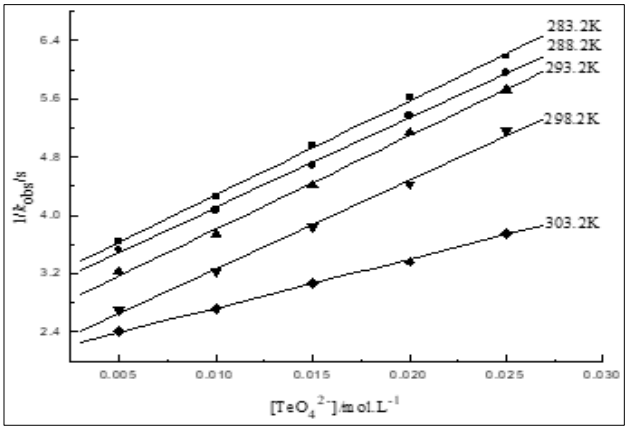


**Fig 5:** Plots of $1/k_{obs}$ versus [$TeO_4^{2-}$] at different temperatures [DTA] = 7.15 × $10^{-4}$ mol·$l^{-1}$; [$OH^-$] = 1.00 × $10^{-2}$ mol·$l^{-1}$; μ = 8.50 × $10^{-2}$ mol·$l^{-1}$; [N-methyldi ethanolamine] = 0.15 mol·$l^{-1}$ ($r \geq 0.998$)

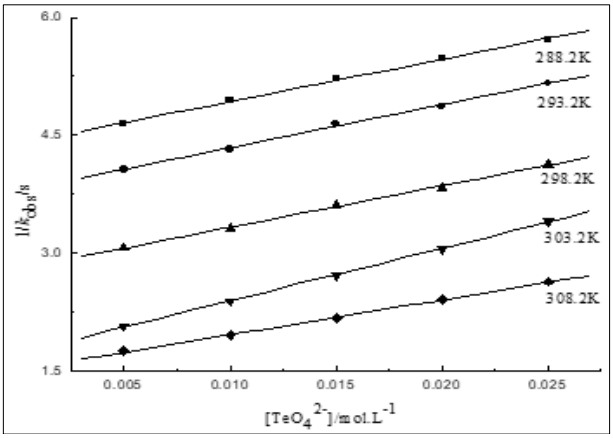


**Fig 6:** Plots of $1/k_{obs}$ versus [$TeO_4^{2-}$] at different temperatures [DTA] = 7.15 × $10^{-4}$ mol·$l^{-1}$; [$OH^-$] = 1.00 × $10^{-2}$ mol·$l^{-1}$; μ = 8.50 × $10^{-2}$ mol·$l^{-1}$; [N,N-dimethyl ethanolamine] = 0.15 mol·$l^{-1}$($r \geq 0.998$)

### 3.4 Rate dependence on μ

At 298.2 K, and constant concentrations of [DTA], [reductant], [$OH^-$], [$TeO_4^{2-}$], the ionic strength was varied from 50 to 150×$10^{-3}$ mol·$l^{-1}$. It was found a negative salt effect in the oxidation of N-methyldiethanolamine and N,N-dimethyl ethanolamine, thus indicating that $k_{obs}$ decreased with the ionic strength [12]. However, the $k_{obs}$ of reductant did not change significantly, this indicated the Ionic strength [13] have nothing influence to the $k_{obs}$ of reductant (Table1).

**Table 1:** Influence of variation of ionic strength μ at 298.2 K.

| μ×$10^3$ (mol· $l^{-1}$) | | 50 | 75 | 100 | 125 | 150 |
|---|---|---|---|---|---|---|
| $k_{obs}$ ×10 /$s^{-1}$ | N-methyldiethanolamine | 3.14 | 3.08 | 2.87 | 2.76 | 2.56 |
| | N,N-dimethyl ethanolamine | 3.10 | 3.03 | 2.83 | 2.57 | 2.49 |

[DTA] = 7.15 × $10^{-4}$ mol·$l^{-1}$; [$OH^-$] = 1.00 × $10^{-2}$ mol·$l^{-1}$; [$TeO_4^{2-}$] = 0.01 mol·$l^{-1}$; [N-methyldi ethanolamine] = 0.15 mol·$l^{-1}$; [N,N-dimethyl ethanolamine] = 0.15 mol·$l^{-1}$.

### 4. Reaction mechanism

In an alkaline medium, the electric dissociation equilibrium of telluric acid was given earlier [13] (p$K_w$=14).

$$H_5TeO_6^- + OH^- \rightleftharpoons H_4TeO_6^{2-} + H_2O \quad \lg\beta_1 = 3.049 \quad (1)$$

$$H_4TeO_6^{2-} + OH^- \rightleftharpoons H_3TeO_6^{3-} + H_2O \quad \lg\beta_2 = -1.00 \quad (2)$$

The distribution of all species of telluride in aqueous alkaline solution can be calculated from equations (1) and (2). In alkaline medium we assume that [$OH^-$] = 1.00 × $10^{-2}$ mol $l^{-1}$, then [$H_4TeO_6^{2-}$]:[$H_5TeO_6^-$]:[$H_3TeO_6^{3-}$] = 1000:89:1, so in the alkaline solution, the $H_5TeO_6^-$ and $H_3TeO_6^{3-}$ species can be neglected, and the main species of telluride is $H_4TeO_6^{2-}$. Based on such distribution and the Rao argument [14], the formula of DTA may be represented by [Ag $(H_4TeO_6)_2]^-$.

Based on the experimental results and discussion, the three plausible mechanisms were proposed as follows: (R stands for N-methyldiethanolamine and N,N-dimethyl ethanolamine)

$$[Ag(H_4TeO_6)_2]^- + OH^- + H_2O \overset{K_1}{\rightleftharpoons} [Ag(H_3TeO_6)(H_2O)_2] + H_4TeO_6^{2-} \quad (3)$$

$$[Ag(H_3TeO_6)(H_2O)_2] + [reductant] \overset{K_2}{\rightleftharpoons} [Ag(H_3TeO_6)(reductant)] + 2H_2O \quad (4)$$

$$[Ag(H_3TeO_6)(reductant)] \xrightarrow[slow]{k} Ag(I) + Products + H_4TeO_6^{2-} \quad (5)$$

Reaction (5) was the rate-determining step, the rate law of the reaction was derived as follows:

$$-d[Ag(III)]_t/dt = k[Ag(H_3TeO_6)(reductant)] \quad (6)$$

Where Ag $(III)_t$ stands for any kind of Ag(III)existing in equilibria (3) (4)and (5), so

$$[Ag(III)]_t = [Ag(H_4TeO_6)_2]^- + [Ag(H_3TeO_6)(H_2O)] + [Ag(H_3TeO_6)(reductant)] \quad (7)$$

According to the equilibrium reaction (3) and (4):

$$K_2 = \frac{[Ag(H_3TeO_6)(reductant)]}{[Ag(H_3TeO_6)(H_2O)][reductant]} \quad (8)$$

$$K_2 = \frac{[Ag(H_3TeO_6)(reductant)]}{[Ag(H_3TeO_6)(H_2O)][reductant]} \quad (9)$$

Based of equations of (7) (8) and (9), obtain: (Reductant)

$$[Ag(H_3TeO_6)(R)] = \frac{K_1K_2[OH^-][R]}{K_1K_2[OH^-][R] + K_1[OH^-] + [H_4TeO_6^{2-}]} \quad (10)$$

Substituting the value of $[Ag(H_3TeO_6)(R)]$ into equation (6) we get the following equation:

$$-d[Ag(III)]_t/dt = \frac{kK_1K_2[R][OH^-]}{K_1K_2[R][OH^-] + K_1[OH^-] + [H_4TeO_6^{2-}]}[Ag(III)]_t = k_{obs}[Ag(III)]_t \quad (11)$$

$$k_{obs} = \frac{kK_1K_2[R][OH^-]}{K_1K_2[R][OH^-] + K_1[OH^-] + [H_4TeO_6^{2-}]} \quad (12)$$

Re-arranging equation (12) leads to equation (13) and (14):

$$\frac{[R]}{k_{obs}} = \frac{[R]}{k} + \frac{[H_4TeO_6^{2-}] + K_1[OH^-]}{kK_1K_2[OH^-]} \quad (13)$$

$$\frac{1}{k_{obs}} = \frac{1+K_2[R]}{kK_2[R]} + \frac{[H_4TeO_6^{2-}]}{kK_1K_2[R]}\frac{1}{[OH^-]} \quad (14)$$

It is evident from equation (11) that the reaction was fraction order for reductant and first order for Ag (Ⅲ). The plots of $k_{obs}$/ [reductant] versus [reductant] were straight lines that have a positive intercept at different temperatures. Equation (14) suggest that the plots of $1/k_{obs}$ versus $1/[OH^-]$ and $1/k_{obs}$ versus $[H_4TeO_6^{2-}]$ were also straight lines, in addition, $k_{obs}$ decreased with the increase of $[H_4TeO_6^{2-}]$ and increased with the increase of $[OH^-]$. Based on equation (13), according to the alue of the intercept, $k_{obs}$ can obtained, Using the transition-state theory, the activation energy and the thermodynamic parameters were evaluated at 298.2 K by the method given earlier [15] (Table2).

**Table 2:** Rate constants (*k*) and activation parameters for the rate-determining step at 298.2 K.

| ***T* (K)** | | **283.2** | **288.2** | **293.2** | **298.2** | **303.2** |
|---|---|---|---|---|---|---|
| *k* ( $s^{-1}$) | N-methyldiethanolamine | 1.10 | 1.29 | 1.48 | 1.65 | 1.90 |
| *T* (K) | | 288.2 | 293.2 | 298.2 | 303.2 | 308.2 |
| *k* × 10 ( $s^{-1}$) | N,N-dimethyl ethanolamine | 2.91 | 4.18 | 5.68 | 7.23 | 9.63 |
| Thermodynamic activation parameters | N-methyldi ethanolamine | $E_a$ (kJ $mol^{-1}$) = 18.35, $\Delta H^{\neq}$ (kJ $mol^{-1}$)= 15.87, $\Delta S^{\neq}$ (J $K^{-1}$ $mol^{-1}$)= -187.59 | | | | |
| | N,N-dimethyl ethanolamine | $E_a$ (kJ $mol^{-1}$) = 42.90, $\Delta H^{\neq}$ (kJ $mol^{-1}$)= 40.42, $\Delta S^{\neq}$ (J $K^{-1}$ $mol^{-1}$)= -114.43 | | | | |

The plots of ln*k* versus 1/*T* have the following intercepts (*a*), slope (*b*) and relative coefficient (*r*):
For N-methyldiethanolamine: *a* = 7.90, *b* = -2206.54, *r* = 0.998, and for N,N-dimethyl ethanolamine:
*a* = 16.70, *b* = -5159.96, *r* = 0.998.

## 5. Conclusions

From the former discussed above the experiment, the rate constants and activation parameters for the reaction have drawn. Through the deep study of the reaction system, it can be good to verify the extraordinary of the transition metal complexes present with low protonated form. Analysing the experiment results, we found the rate constant for N-methyldiethanolamine is larger than N,N-dimethyl ethanolamine in alkaline environment, this because there are two hydroxyl group in N-methyldiethanolamine and in the N,N-dimethyl ethanolamine exists only one. In alkaline medium the hydroxyl group be more likely to lose the hydrogen atom become to oxygen anions, then via a oxidation reaction the oxygen anions convert to carbonyl group. So the rate of reaction in proportion to the concentration of hydroxyl ions. In addition, there is an obvious negative salt effect in the oxidation of N-methyldiethanolamine and N,N-dimethyl ethanolamine , because the rate of the reaction is markedly influenced by the migration rate of activated complex. The migration rate markedly decreases with the increase of the steric hindrance from the reductant. The volume of N-methyldiethanolamine and N,N-dimethyl ethanolamine is larger, so the effect of steric hindrance to it is obvious, and the migration rate of activated complex become lower. The rate of the reaction is in inverse proportion to ionic strength. The mechanisms described are consistent with experiment results and kinetic results.

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