

# Oxidation of Triethylamine by Ferricyanide Ions in the Presence of Sodium Hydroxide and Potassium Hydroxide

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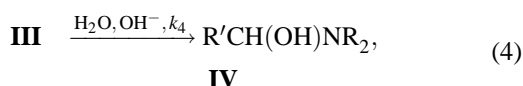
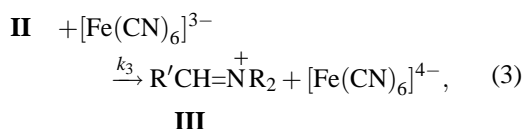
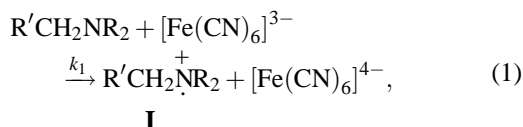
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The rate of the oxidation of triethylamine by ferricyanide ions in sodium hydroxide or potassium hydroxide solutions has been determined spectrophotometrically at 25 °C. Analysis of the kinetic data indicates that the hydroxide ion does not appear in the rate law. Strong retardation of the oxidation of triethylamine, caused by the addition of ferrocyanide ions, has been observed. A plausible mechanism is suggested, and a suitable rate law, congruent with the experimental observations, has been derived.

**Key words:** Triethylamine; Potassium Ferricyanide; Potassium Ferrocyanide; Sodium Hydroxide; Potassium Hydroxide; Polarization and Solvation.

## 1. Introduction

Aliphatic tertiary amines can be oxidized by a variety of reagents [1 – 7]. The structure of these amines and the redox potential of the oxidant control the products and rates of oxidation. Detailed studies of many of these oxidation reactions have used potassium ferricyanide as the oxidizing agent [8]. It has been suggested that the oxidizing species react with electron-rich organic compounds via abstraction of one electron [9]. A detailed mechanism of the oxidation of trialkylamines by alkaline potassium ferricyanide has been reported [3, 4]:



The rate law derived from the above mechanism, by applying the steady-state approximation, is

$$-d[\text{Fe}(\text{CN})_6^{3-}]/dt = 2k_1[\text{Fe}(\text{CN})_6^{3-}][\text{amine}]. \quad (6)$$

The oxidation reaction was found to be reversible and was confirmed by addition of potassium ferrocyanide to the oxidation reaction [2, 6]. In addition, a cationic salt effect [3, 9] was observed in the oxidation of tertiary amines. Swinehart [10] and others [11 – 12] have interpreted this cationic effect by assuming that the cation acts as a bridge for the electron transfer.

However, the effect of hydroxide ions on the oxidation reaction has not received enough attention. The only study [3] deals with the dependence of the rate constant on sodium hydroxide was performed in the concentration range 0.0 – 0.5 M. The effect has been attributed to the sodium cation acting as a bridge for the electron abstraction.

The present study was undertaken to investigate the dependence of the rate of the oxidation of triethylamine on the concentration of the hydroxide ion. The effect of the hydroxide ion and the mechanism of the oxidation of triethylamine are discussed.

## 2. Experimental

Potassium ferrocyanide, potassium ferricyanide (Fischer), sodium hydroxide, potassium hydroxide, acrylonitrile and triethylamine (Aldrich) were analar reagents and were used without further purification. The concentrations of the sodium and potassium

hydroxide solutions were determined by titration with standard potassium hydrogen phthalate. The concentration of triethylamine was determined by titration against standardized hydrochloric acid. The water used throughout was deionized and freshly redistilled from  $\text{KMnO}_4/\text{NaOH}$ . This water was degassed for 0.5 h and then saturated with nitrogen.

### 3. Kinetic Measurements

The kinetics were followed by measuring the absorbance of ferricyanide at 420 nm. The absorbance spectra were recorded using a Varian/Cary 2390 Spectrophotometer, connected to a data station (Varian DS-15). In each experiment, 3 ml of alkaline triethylamine solution ( $2.0 \cdot 10^{-2}$  M) were placed in a thermostated quartz cell, and then a 5  $\mu\text{l}$  aliquot of stock solution ( $3.0 \cdot 10^{-1}$  M) of potassium ferricyanide was injected into the quartz cell. After rapid mixing, the absorbance of the solution was measured at appropriate intervals. The results were stored by using the kinetic storage program (Varian 85-180080-00). Only the initial portion of the reaction ( $t_{0.7}$ ) was followed to minimize any retarding effect of ferrocyanide formed. The pseudo-first-order rate constants ( $k_{\text{obs}}$ ) were calculated using a kinetic calculation program (Varian 85-180080-00) and were found to be of first-order with correlation coefficients higher than 0.99.

### 4. Results and Discussion

A number of runs with constant initial concentration of triethylamine, ferricyanide ions and different

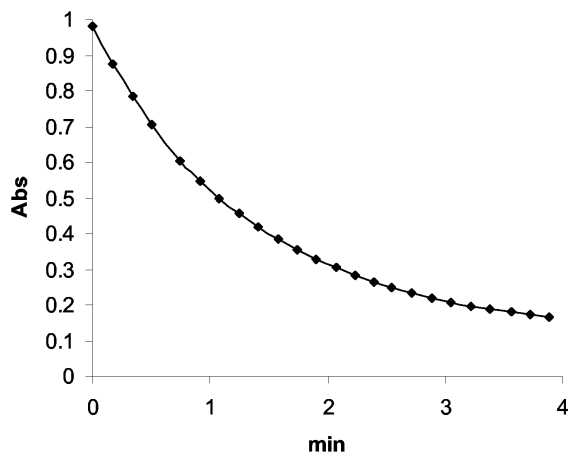


Fig. 1. Variation of the absorbance versus time for oxidation of triethylamine by potassium ferricyanide in aqueous 0.5 M NaOH. The solid line represents  $A_t = (A_0 - A_\infty)e^{-kt} + A_\infty$ .

Table 1. The pseudo-first-order rate constants ( $k_{\text{obs}}$ ) for the oxidation of triethylamine ( $2.0 \cdot 10^{-2}$  M) by potassium ferricyanide ( $5.0 \cdot 10^{-4}$  M) in aqueous sodium hydroxide and potassium hydroxide solutions at  $(25 \pm 0.1)^\circ\text{C}$ .

[MOH], M	$k_{\text{obs}} \cdot 10^4 \text{ s}^{-1}$	
	NaOH	KOH
3.0	$398.2 \pm 0.9$	$548.1 \pm 1.1$
2.5	$368.5 \pm 0.7$	$486.6 \pm 0.9$
2.0	$316.3 \pm 0.6$	$418.3 \pm 0.8$
1.5	$266.1 \pm 0.4$	$354.2 \pm 0.6$
1.0	$197.1 \pm 0.4$	$263.1 \pm 0.5$
0.75	$168.2 \pm 0.3$	$232.1 \pm 0.3$
0.5	$116.5 \pm 0.4$	$153.1 \pm 0.2$
0.25	$74.4 \pm 0.2$	$96.4 \pm 0.4$
0.1	$45.3 \pm 0.3$	$52.3 \pm 0.2$
0.05	$25.1 \pm 0.2$	$32.3 \pm 0.3$
0.03	$19.4 \pm 0.2$	$26.2 \pm 0.2$
0.01	$13.4 \pm 0.1$	$17.2 \pm 0.2$
0.0	$6.8 \pm 0.1$	$6.8 \pm 0.1$

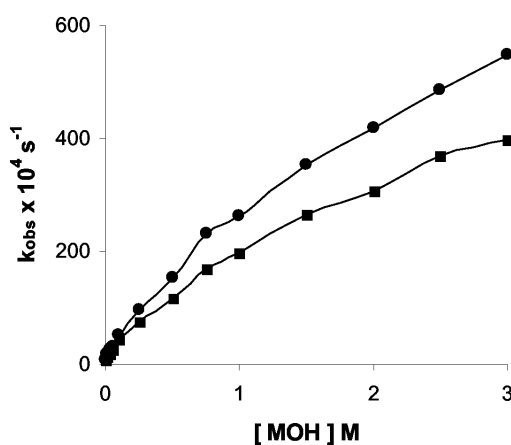


Fig. 2. Plots of  $k_{\text{obs}}$  versus [MOH] for oxidation of triethylamine in aqueous sodium hydroxide (■) and potassium hydroxide (●) at  $(25 \pm 0.1)^\circ\text{C}$ .

concentrations of sodium hydroxide or potassium hydroxide solutions were carried out at  $(25 \pm 0.1)^\circ\text{C}$  in aqueous media. Figure 1 displays a typical run showing the variation of the absorbance of the ferricyanide ion with time. This oxidation reaction follows the simple kinetic relationship shown in the equation

$$-d[\text{Fe}(\text{CN})_6^{3-}]/dt = k_{\text{obs}}[\text{Fe}(\text{CN})_6^{3-}]. \quad (7)$$

The rate constants of oxidation of triethylamine in various solutions of sodium and potassium hydroxides are recorded in Table 1 and shown in Figure 2. The results clearly indicate, first, the rate constants increase with the increase of hydroxide concentration. As previously suggested [3, 9, 11–14], this could be due to a catalytic effect of NaOH or KOH by binding of al-

kali metal ions to the oxidants; the hydroxide ion might act as a specific catalyst. Second, the rate constants in the presence of potassium hydroxide are higher than the corresponding values in the presence of sodium hydroxide. This might be due to one or more of the following reasons. First, the degree of dissociation of sodium and potassium hydroxide at high concentrations could not be the same because ionic strength will not be the same. Second, the solvation number [15, 16] of  $\text{Na}^+$  is higher than that for  $\text{K}^+$ . Third, the polarizability of  $\text{K}^+$  is higher than that of [17].

Assuming that the cation or the hydroxide ion acts as a specific catalyst, the rate law for the oxidation of the triethylamine by the ferricyanide ion can be written as

$$\text{Rate} = k_o[\text{Fe}(\text{CN})_6^{3-}][(\text{C}_2\text{H}_5)_3\text{N}][\text{M}^+] \text{ or } [\text{OH}^-], \quad (8)$$

where  $k_o$  is the third-order rate constant at zero ionic strength. To show whether the concentration of  $[\text{M}^+]$  or  $[\text{OH}^-]$  affects the rate, (8) can be written as:

$$\text{Rate} = k_{\text{obs}}[\text{Fe}(\text{CN})_6^{3-}]. \quad (9)$$

The observed rate constant,  $k_{\text{obs}}$ , and the second-order rate constant,  $k_f$ , are given by (10) and (11):

$$k_{\text{obs}} = k_o[(\text{C}_2\text{H}_5)_3\text{N}][\text{M}^+] \text{ or } [\text{OH}^-], \quad (10)$$

$$k_f = k_{\text{obs}}/[(\text{C}_2\text{H}_5)_3\text{N}] = k_o[\text{M}^+] \text{ or } [\text{OH}^-]. \quad (11)$$

Equation (11) can be written as

$$\log k_f = \log k_o + n \log [\text{M}^+] \text{ or } [\text{OH}^-]. \quad (12)$$

At this point it is necessary to include the effect of ionic strength on the rate constant between ions in aqueous solutions at 25 °C [18, 20–23]. As a result, (12) becomes

$$\log k_f = \log k_o + n \log [\text{M}^+] \text{ or } [\text{OH}^-] + 1.02 Z_1 Z_2 u^{1/2} / (1 + u^{1/2}) + bu, \quad (13)$$

where  $n$  is the order of  $[\text{M}^+]$  or  $[\text{OH}^-]$ ,  $Z_1$  and  $Z_2$  are the charges of the reactants;  $u$  is the ionic strength and  $b$  a free parameter, which could be positive or negative. The results (Table 1) are correlated in (13). The values of  $Z_1 Z_2$ ,  $b$  and  $k_o$  are reported in Table 2. The values of  $k_o$  are slightly higher than  $k_f$  in water, and  $Z_1 Z_2$  is less than +3 in the presence of sodium and potassium hydroxides. The calculated order,  $n$  of  $[\text{M}^+]$  or  $[\text{OH}^-]$

Table 2. Calculated kinetic parameters from using different equations of oxidation of triethylamine by ferricyanide ion.

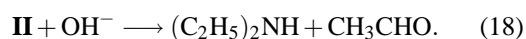
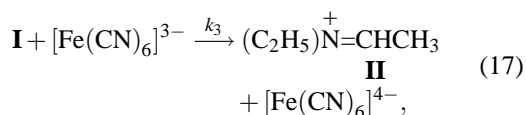
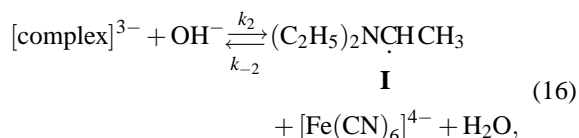
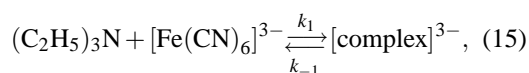
$[\text{OH}^-]$	NaOH	KOH
<i>Equation (12)</i>		
Intercepts	$2.74 \pm 0.03$	$2.83 \pm 0.02$
$k_o \cdot 10^4$	18.2	14.8
$n^a$	$0.17 \pm 0.02$	$0.09 \pm 0.01$
$Z_1 Z_2$	$2.13 \pm 0.04$	$2.57 \pm 0.03$
$-b \cdot 10^2$	$3.7 \pm 0.03$	$4.6 \pm 0.02$
$R^b$	0.9992	0.9997
S.e.r. <sup>c</sup> · 10 <sup>2</sup>	2.5	1.6
<i>Equation (13)</i>		
Intercepts	$3.10 \pm 0.06$	$3.04 \pm 0.05$
$k_o \cdot 10^4$	7.9	9.1
$Z_1 Z_2$	2.71	2.83
$R^b$	0.997	0.996
S.e.r. <sup>c</sup> · 10 <sup>2</sup>	4.0	5.7

<sup>a</sup> Order of  $[\text{M}^+]$  or  $[\text{OH}^-]$ . <sup>b</sup> Correlation coefficients. <sup>c</sup> Standard error of estimate.

is less than 0.2. This might indicate that the hydroxide ion or  $\text{M}^+$  acts as a specific catalyst in the oxidation of triethylamine without appearing in the rate law. The  $b$  values are small. According to Davis [23] a slope smaller than 0.20  $Z_1 Z_2$  or negative, show that ion-pair formation takes place. Since the order of  $[\text{M}^+]$  or  $[\text{OH}^-]$  and the values of  $b$  are small, the  $[\text{M}^+]$  or  $[\text{OH}^-]$  and  $bu$  are neglected. Therefore, (13) is reduced to

$$\log k_f = \log k_o + 1.02 Z_1 Z_2 u^{1/2} / (1 + u^{1/2}). \quad (14)$$

In this case,  $k_o$  is the second-order rate constant at zero ionic strength. This will leave a linear relationship between  $\log k_f$  and  $u^{1/2} / (1 + u^{1/2})$ . This is shown in Figure 3. In the light of the above-mentioned results, the following mechanism for the oxidation reaction of triethylamine by the ferricyanide ion in the presence of the hydroxide ion is suggested:



K <sub>4</sub> [Fe(CN) <sub>6</sub> ], 10 <sup>3</sup> M	1.0 M NaOH	1.0 M KOH	<i>k</i> <sub>obs</sub> · 10 <sup>4</sup> s <sup>-1</sup>				H <sub>2</sub> O
			0.5 M NaOH	0.5 M KOH	0.1 M NaOH		
0.0	197.1 ± 0.4	263.1 ± 0.5	116.5 ± 0.4	153.1 ± 0.2	45.3 ± 0.3		6.8 ± 0.1
1.0	188.2 ± 0.5	257.5 ± 0.6	109.1 ± 0.2	146.5 ± 0.4	32.7 ± 0.4		3.7 ± 0.2
2.0	181.3 ± 0.3	252.0 ± 0.4	97.9 ± 0.3	139.5 ± 0.4	24.1 ± 0.4		2.6 ± 0.1
3.0	177.0 ± 0.4	246.9 ± 0.3	91.2 ± 0.3	133.7 ± 0.5	21.2 ± 0.3		2.0 ± 0.2
4.0	170.1 ± 0.2	241.8 ± 0.4	84.7 ± 0.2	129.0 ± 0.2	17.8 ± 0.2		1.6 ± 0.1
5.0	162.9 ± 0.2	237.1 ± 0.2	81.3 ± 0.1	123.0 ± 0.3	15.2 ± 0.2		1.4 ± 0.1
7.0	155.8 ± 0.3	228.0 ± 0.2	74.8 ± 0.1	116.3 ± 0.1	12.5 ± 0.3		1.1 ± 0.1
10.0	143.7 ± 0.1	215.7 ± 0.1	65.0 ± 0.3	104.5 ± 0.2	9.3 ± 0.2		0.8 ± 0.1
15.0	132.0 ± 0.2	197.9 ± 0.1	53.9 ± 0.1	87.5 ± 0.2	6.8 ± 0.2		0.6 ± 0.1
20.0	121.1 ± 0.1	182.3 ± 0.1	45.5 ± 0.2	76.8 ± 0.1	5.3 ± 0.1		0.4 ± 0.1

Table 3. The dependence of observed rate constants, *k*<sub>obs</sub>, of oxidation of triethylamine (2.0 · 10<sup>-2</sup> M) by potassium ferricyanide (5.0 · 10<sup>-4</sup> M) in aqueous sodium hydroxide and potassium hydroxide solutions in presence of potassium ferrocyanide at (25 ± 0.1) °C.

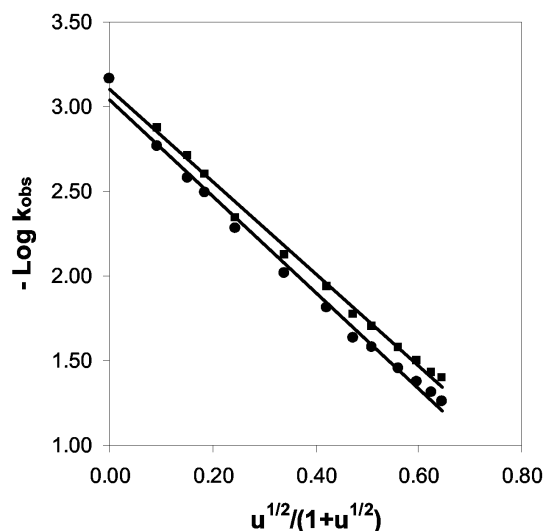


Fig. 3. Plots of log *k*<sub>obs</sub> versus *u*<sup>1/2</sup>/(1 + *u*<sup>1/2</sup>) for oxidation of triethylamine in aqueous sodium hydroxide (■) and potassium hydroxide (●) at (25 ± 0.1) °C.

The first step is reversible and involves the formation of a complex, similar to what has been previously suggested in the mechanism of oxidation of triethanoldiamine by the alkaline ferricyanide ion [24]. Application of the steady-state approximation and deleting the small terms gives the rate law

$$\text{Rate} = \frac{k_1 k_2 k_3 [(C_2H_5)_3N][Fe(CN)_6^{3-}][OH^-]}{k_{-1} k_2 [Fe(CN)_6^{4-}] + k_2 k_3 [OH^-]}. \quad (19)$$

The first term in the denominator of this equation is smaller than the second term, therefore it can be canceled and (19) becomes

$$\text{Rate} = k_1 [(C_2H_5)_3N][Fe(CN)_6^{3-}]. \quad (20)$$

The reversibility of the reaction was investigated by studying the effect of addition of potassium ferrocyanide, [Fe(CN)<sub>6</sub>]<sup>4-</sup>, on the reaction rate at different concentrations of KOH, NaOH and also in water

Table 4. The slopes and intercepts of the plot of 1/*k*<sub>obs</sub> against [K<sub>4</sub>Fe(CN)<sub>6</sub>] of oxidation of triethylamine in aqueous sodium hydroxide, potassium hydroxide or water.

[MOH]	Slopes	Intercepts	<i>k</i> <sub>1</sub> · 10 <sup>4</sup>	$\frac{k_{-1}k_{-2}}{k_2k_3}$	<i>R</i>	S.e.r
1.0 M NaOH	1584 ± 3	52.2 ± 0.6	191.6	30.3	0.995	0.9
1.0 M KOH	842 ± 1	38.0 ± 0.2	263.2	22.2	0.9996	0.3
				6		
0.5 M NaOH	6577 ± 2	88.2 ± 0.7	113.4	37.3	0.998	0.7
0.5 M KOH	3246 ± 2	64.8 ± 0.4	154.3	25.0	0.9992	0.4
				2		
0.1 M NaOH	82967 ± 32	230.7 ± 0.6	43.3	35.9	0.9992	0.6
				2		
H <sub>2</sub> O <sup>a</sup>	11154 · 10 <sup>2</sup> ± 4	1494.3 ± 8	6.7	7.5 · 10 <sup>-5</sup>	0.996	0.9

<sup>a</sup> The pH value was assumed to be 7.

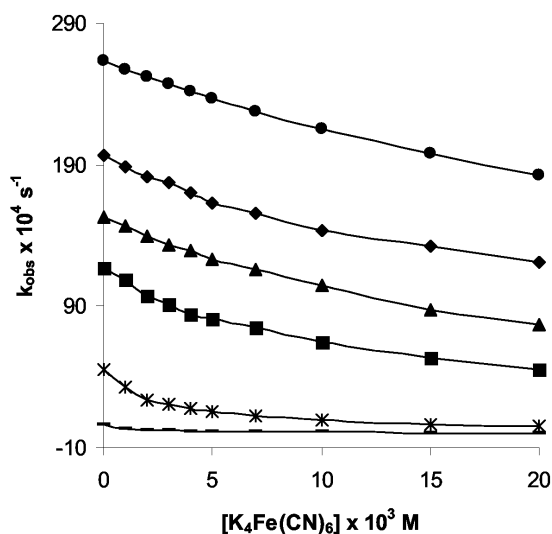


Fig. 4. The effects of added potassium ferrocyanide on *k*<sub>obs</sub> of oxidation of triethylamine in 1.0 M NaOH (◆), 1.0 M KOH (●), 0.5 M NaOH (■), 0.5 M KOH (▲), 0.1 M NaOH (×) and water (○).

at (25 ± 0.1) °C. The results are reported in Table 3 and displayed in Figure 4. A substantial retardation of the rate constant was observed by addition of potas-

sium ferrocyanide. In this case, the first term in the denominator of (19) can not be cancelled. Therefore, the second-order constant,  $k_j$ , is given by

$$k_j = k_1 k_2 k_3 [\text{OH}^-] / (k_{-1} k_2 [\text{Fe}(\text{CN})_6^{4-}] + k_2 k_3 [\text{OH}^-]). \quad (21)$$

Fitting  $1/k_j$  in (21) versus the concentration of  $\text{K}_4[\text{Fe}(\text{CN})_6]$  (Table 3) gives a straight line. The slope and intercept are equal to  $k_{-1} k_2 / (k_1 k_2 k_3 [\text{OH}^-])$  and  $1/k_1$ , respectively. The calculated values of  $k_1$  is nearly equal to  $k_j$  at zero concentration of  $\text{K}_4[\text{Fe}(\text{CN})_6]$ . The values of the slopes and intercepts are listed in Table 4.

A further investigation, similar to the work of Mucientes [25], has also provided evidence for the existence of radical intermediate. When acrylonitrile (0.1 M) was added to the reaction mixture, large amounts of a polymeric product were formed after a few minutes, except in water, where a longer time was needed. However, this polymeric product did not form

in the absence of triethylamine. This indicates the formation of a free radical in the oxidation reaction of triethylamine.

Finally, the differences in the observed rate constants of oxidation of triethylamine in potassium hydroxide and sodium hydroxide may be due to the following: The ion-pair formation in sodium hydroxide is more pronounced than in potassium hydroxide. The value of  $Z_1 Z_2$  (Table 2) in the presence of potassium hydroxide is slightly higher than that for sodium hydroxide. This might support our conclusion that the ion-pair formation in sodium hydroxide is more important than that in potassium hydroxide. The solvation number of  $\text{Na}^+$  is higher than that for  $\text{K}^+$ . As a result, the mobility of  $\text{Na}^+$  is smaller than that of  $\text{K}^+$ .

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