Lawrence Berkeley National Laboratory
Recent Work

**Title**
THE REACTION OF FERRICYANIDS WITH BCPHYDRIDE IN AQUEOUS SOLUTION

**Permalink**
https://escholarship.org/uc/item/1ms3p93r

**Author**
Hsu, Lydia S.

**Publication Date**
1964
THE REACTION OF FERRICYANIDE WITH BOROHYDRIDE IN AQUEOUS SOLUTION

Berkeley, California
DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.
THE REACTION OF FERRICYANIDE WITH BOROHYDRIDE IN AQUEOUS SOLUTION

Lydia S. Hsu
(M.S. Thesis)

January 1964

Reproduced
by the
Technical Information Division directly from author's copy.
THE REACTION OF FERRICYANIDE WITH BOROHYDRIDE IN AQUEOUS SOLUTION

CONTENTS

ABSTRACT ........................................ iii
I. Introduction ..................................... 1
II. Experimental
   A. Preparation of Solutions ..................... 5
   B. Reaction in Glass Beaker ...................... 5
   C. Reaction in Wax-Coated Beaker ............... 12
   D. Surface Catalytic Effect in Low Concentration
      region -- Check of Freund's Results ........ 16
III. Results and Discussion ....................... 20
Acknowledgments ................................... 23
References ....................................... 24
THE REACTION OF FERRICYANIDE WITH BOROHYDRIDE IN AQUEOUS SOLUTION

Lydia S. Hsu

Lawrence Radiation Laboratory
and Department of Chemistry
University of California
Berkeley, California

ABSTRACT

The kinetics of the reaction of ferricyanide with borohydrider (in the concentration ranges for both reactants of 0.1-0.5M) has been studied in alkaline aqueous solution at room temperature. The reaction was found to be catalyzed by glass surfaces. This catalysis, however, can be avoided by using wax-coated-surfaces. The rate of change of the hydroxide ion concentration was found to be first order in both ferricyanide and borohydrider and independent of the hydroxide ion, at least in the high pH region, with a rate constant of \(4.93 \times 10^{-4} \text{M}^{-1} \text{min}^{-1}\). This result is different from that found by Freund for very dilute ferricyanide and borohydrider ion in buffered aqueous solution. Under the conditions of Freund's experiments, no glass catalysis was observed.
THE REACTION OF FERRICYANIDE WITH DOROHYDRIE
IN AQUEOUS SOLUTION

Lydia S. Hsu

Lawrence Radiation Laboratory
and Department of Chemistry
University of California
Berkeley, California

I. INTRODUCTION

The recent study of complex hydrides of boron, aluminum and
gallium is one of the most important developments in inorganic
chemistry in view of the broad usefulness of these compounds as
reducing agents. In the process of complex ion formation, the
hydride ion coordinates, or donates a share in its pair of
electrons to the central atom of the acceptor molecule:

\[ \text{H}^- + \text{XH}_4^- \rightleftharpoons \text{H}^+ \cdot \text{XH}_3^- \cdot \text{H}^+ \]

(1)

where X = B, Al or Ga. Since the hydride ion is not a strong
electron donor, the acceptor component must necessarily be strong
if compound formation is to take place. All of these XH\text{4}^- ions
are believed to be tetrahedral, i.e., the four bonds to the
hydrogen atoms are equivalent. This structure has been
established for the BH\text{4}^- ion.\textsuperscript{1,2} The stability of a complex
hydride salt depends not only on the strength of the electron
acceptor but also on the strength of the metallic component as an electron acceptor. The alkali metal borohydrides are fairly stable since the alkali metal ion can offer very little competition to the BH$_3$ group for the electron associated with hydride ion. The salts most widely used as reducing agents are NaBH$_4$ and KBH$_4$.

The reactions of borohydride with iodine, permanganate and hypochlorite in aqueous solution have been investigated from an analytical standpoint by Jensen. Several other reactions of borohydride have been surveyed by other workers. However, water is the first inorganic oxidising agent for borohydride which has been studied kinetically. In this case, the rate of the hydrolysis of borohydride may be represented by the expression:

$$-\frac{d[OH^-]}{dt} = k_1[H^+](BH_4^-) + k_2(BH_4^-)$$

over the pH ranges 3.8-14. The rate-determining step of the acid hydrolysis is believed to be the formation of a short-lived intermediate, BH$_5$,

$$BH_4^- + H^+ \xrightarrow{\text{slow}} BH_5$$

followed by,

$$BH_5 \rightarrow BH_3 + H_2$$

In order to get more information of the general behavior of borohydride as a reducing agent, it seems worthwhile to do extensive investigation of the kinetics of the redox reactions of borohydride with other inorganic species. Among them, the ferri-
cyanide ion should be an attractive choice because both ferri-
cyanide and ferrocyanide are extremely stable with respect to
dissociation and have the same octahedral geometry and chemical
composition. Therefore, we can expect that only a one-electron
transfer is involved. The reaction of borohydride with ferri-
cyanide to give borate and ferrocyanide has been previously
studied in buffered aqueous solution by Freund. The con-
centration ranges in his experiments were: initial borohydride
from \(1 \times 10^{-3}\) to \(70 \times 10^{-3} \text{M}\), ferricyanide from \(1.5 \times 10^{-4}\) to \(18 \times 10^{-4} \text{M}\)
and hydrogen ion from \(6 \times 10^{-10}\) to \(3 \times 10^{-3} \text{M}\). The over-all
stoichiometry is,

\[
8\text{Fe(CN)_3}^- + \text{BH}_4^- + 8\text{OH}^- \rightarrow 8\text{Fe(CN)_4}^4^- + \text{H}_2\text{BO}_3^- + 5\text{H}_2\text{O} \quad (5)
\]

The rate of disappearance of the ferricyanide ion was measured
from its absorption with a spectrophotometer to be first order
in both borohydride and hydrogen ion and independent of the
ferricyanide ion,

\[
- \frac{d(\text{Fe(CN)_3}^-)}{dt} = k(\text{BH}_4^-)(\text{H}^+). \quad (6)
\]

This kinetics suggests that the activated complex for the rate-
determining step of the oxidation of borohydride by ferricyanide
is probably the same as the hydrolysis, in the absence of
ferricyanide, of borohydride alone.

While extending to higher concentration ranges of both boro-
hydride and ferricyanide in alkaline aqueous solutions, however,
it was found in this laboratory that obvious deviation in rate
law of this redox reaction from that of dilute concentration case occurred. Several observations from preliminary experiments were: (i) the reaction was quite unreproducible without stirring; (ii) the rate of change of hydroxide ion concentration with excess borohydride and ferricyanide ion increased with increasing ferri-cyanide ion concentration; and (iii) the glass-surface catalytic effect was extremely influential. Therefore, more work has been done on these aspects. The results showed that a different mechanism must exist.
II. EXPERIMENTAL

A. Preparation of Solutions

Metal Hydrides potassium borohydride (KBH₄ > 97%) was used without further purification. It is a white crystalline material which is stable in dry air. General Chemical potassium ferricyanide (K₃Fe(CN)₆ > 99%) was recrystallized from water and dried under vacuum at room temperature. The aqueous solution of ferricyanide thus obtained was slightly acidic because of dissolved carbon dioxide. Both solid reactants were separately dissolved in 0.01 M sodium hydroxide up to 100 ml., in order to stabilize the borohydride and to get roughly the same initial hydroxide ion concentrations. These two solutions were then mixed together in a 400 ml. beaker with vigorous stirring, especially at the beginning of mixing.

In these experiments, the ferricyanide and borohydride ion concentrations were kept essentially constant by using a large excess, i.e., both of them from 0.1 to 0.5 M while initial hydroxide ion was 1.4 x 10⁻² to 2.4 x 10⁻² M.

B. Reaction in Glass Beaker

a. Reaction without Stirring in an Open Vessel

The kinetic studies were carried out at room temperature by continuously following the concentration of hydroxide ion with a Radiometer pH meter, using a Type G222B glass electrode. A Radiometer Type S1001 buffer solution (pH = 6.50) was used as
a pH standard.

When the reaction mixture was allowed to stand still after bringing the two reagents together, quite peculiar and unreproducible results were obtained. The pH value of the solution dropped slowly until it reached somewhere around 8 to 9 after a period of time which varied from a few seconds to one hour from the start of the reaction, then a spontaneous foaming occurred. After the foaming, the solution became acidic. An example of these unreproducible results was shown in Fig. 1. In fact, it was this observation which led to the performance of this work. Such phenomena were not expected if the reactions were the same as that reported by Freund for the low concentration case.

b. Reaction with Stirring in an Open Vessel

When the reaction proceeded with constant stirring in a glass beaker, a more satisfactory result was obtained. Typical runs were shown in Fig. 2. The hydroxide ion concentration vs. time plot was linear in the high concentration region, but began to curve toward the time axis after a turning point was reached. This point occurred at an approximate hydroxide ion concentration of \(5 \times 10^{-3}\) to \(7 \times 10^{-3}\) M in all runs with different ferricyanide and borohydride concentration. Spontaneous foaming followed as before.

The linear relationship in high concentration region indicated a zero order with respect to hydroxide ion of the reaction. It was also noticed that, with constant borohydride, \(-d(OH^-)/dt\)
Fig. 1. pH vs. time for reactions in glass beakers without stirring. Both runs at the same concentrations, \((BH_4^-) = 0.05 M\), \((Fe(CN)_6^{3-}) = 0.15 M\).
Fig. 2. (OH⁻) vs. time for reactions in glass beakers with stirring.
increased almost twice when ferricyanide was doubled. Neither of these observations could be explained by Freund's rate equation which suggested that \(-d(OH^-)/dt = -d(Fe(CN)_6^{3-})/dt\) should be first order in hydrogen ion and zero order in ferri-cyanide.

Furthermore, the lack of reproducibility mentioned before still remained, even though the ambiguity was greatly minimized by stirring of the solution. Therefore, we tried to study other possible effects which might be involved in this reaction.

c. Reaction with Exclusion of Air

Since this kinetic study was made by following the pH value of the solution, experimental error might be caused by the atmospheric carbon dioxide which dissolved into the solution if an open vessel was used. To test this, pure argon gas was blown over the top of the solution and the result thus obtained was compared with that of the reaction with solution directly contacted with air. Since argon gas is more dense than air, the solution could be isolated from air. As shown in Fig. 3, the rate of change of hydroxide ion was decreased for a small amount with exclusion of air by this method. A same result was obtained for an alkaline solution without any borohydride and ferricyanide in it. The \(-d(OH^-)/dt\) due to air alone was of the order of \(2 \times 10^{-5}\) M min\(^{-1}\). However, since this value was small when compared to the observed total rate, this effect could be neglected for the first approximation.
d. **Surface Catalytic Effect**

Surface catalysis was first noticed by observing that bubbles formed with a varied rate on the wall of the glass beaker during the reaction without stirring. The situation was improved by using constant stirring of the solution. The bubbles on the wall disappeared. This might be connected to the difference of observations between reactions with and without stirring. However, it would be expected that surface catalysis still existed as long as a glass beaker was used. Therefore, experiments in containers with paraffin (wax-coated) and polyethylene surfaces were performed. Positive evidence was found that the reaction rates changed drastically for different types of surfaces. A qualitative result was listed in Table 1 for comparison.

<table>
<thead>
<tr>
<th>Types of Surfaces</th>
<th>$-\frac{d[OH^-]}{dt}$ (M min$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glass</td>
<td>~13x10$^{-5}$</td>
</tr>
<tr>
<td>Polyethylene</td>
<td>~4x10$^{-5}$</td>
</tr>
<tr>
<td>Paraffin (wax-Coated)</td>
<td>~1x10$^{-5}$</td>
</tr>
</tbody>
</table>
C. Reaction in Wax-Coated Beaker

As shown in Table 1, a wax-coated surface had the least catalytic effect. A series of experiments was done for different ferricyanide and borohydride ion concentrations in wax-coated beakers. American Oil Parawax wax was used. Since the reaction rates ranged from $1 \times 10^{-5}$ to $12 \times 10^{-5}$ M min$^{-1}$ in this whole series, the exclusion of air became more important. Therefore, argon gas protection for the solutions was used for all runs. To make sure that no reactions existed had contributions to the $-d(\text{OH}^-)/dt$ term other than the true reaction between ferricyanide and borohydride, several preliminary checks have been done.

Three kinds of solutions including (i) $(\text{BH}_4^-) = 0$, $(\text{Fe(CN)}_6^{3-}) = 0$, $(\text{OH}^-) = 10^{-2}$ M; (ii) $(\text{BH}_4^-) = 0$, $(\text{Fe(CN)}_6^{3-}) = 0.3$ M, $(\text{OH}^-) = 10^{-2}$ M; and (iii) $(\text{BH}_4^-) = 0.3$ M, $(\text{Fe(CN)}_6^{3-}) = 0$, $(\text{OH}^-) = 10^{-2}$ M were observed for two hours and no appreciable change in the hydroxide ion concentration was found in either of the three cases. These implied that (i) the wax surface had no active impurity; (ii) the exclusion of air was complete; (iii) the ferricyanide was very stable; and (iv) the hydrolysis of borohydride in this high pH region had no contribution to the $-d(\text{OH}^-)/dt$ term.

This series included different runs with both ferricyanide and borohydride from 0.1 to 0.5 M and initial hydroxide ion from $1.4 \times 10^{-2}$ to $2.4 \times 10^{-2}$ M.

The typical $(\text{OH}^-)$ vs. time plot for all runs as shown in Fig. 4 showed the same tendency as seen before in glass beaker runs.
It was linear in high (OH\(^{-}\)) region and began to curve toward the time axis once a turning point, (OH\(^{-}\))\(_t\), was reached.

For the linear part, the slopes which gave the values of \(-d(OH^-)/dt\) showed definitely first order dependence of the reaction rate on both ferrocyanide and borohydride and zero order on hydroxide ion. This relation was obtained by comparing the lines with the equation,

\[
-\frac{d(OH^-)}{dt} = 4.93 \times 10^{-4}(BH_4^-)(Fe(CN)_6^{3-})
\]  

and the experimental results (Table 2) in Fig. 5 and Fig. 6. These slopes could be reproduced.

Table 2. Experimental Values of \(-d(OH^-)/dt\) and (OH\(^{-}\))\(_t\).

<table>
<thead>
<tr>
<th>((BH_4^-))</th>
<th>((Fe(CN)_6^{3-}))</th>
<th>(-d(OH^-)/dt \times 10^5)</th>
<th>((OH^-)_t \times 10^5)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.500</td>
<td>0.500</td>
<td>12.20</td>
<td>7.0</td>
</tr>
<tr>
<td>0.500</td>
<td>0.250</td>
<td>5.90</td>
<td>5.3</td>
</tr>
<tr>
<td>0.500</td>
<td>0.150</td>
<td>3.85</td>
<td>-</td>
</tr>
<tr>
<td>0.500</td>
<td>0.100</td>
<td>2.75</td>
<td>-</td>
</tr>
<tr>
<td>0.300</td>
<td>0.500</td>
<td>7.50</td>
<td>6.2</td>
</tr>
<tr>
<td>0.300</td>
<td>0.375</td>
<td>5.60</td>
<td>-</td>
</tr>
<tr>
<td>0.300</td>
<td>0.250</td>
<td>3.80</td>
<td>7.0</td>
</tr>
<tr>
<td>0.200</td>
<td>0.500</td>
<td>4.95</td>
<td>6.2</td>
</tr>
<tr>
<td>0.200</td>
<td>0.250</td>
<td>2.25</td>
<td>-</td>
</tr>
<tr>
<td>0.200</td>
<td>0.150</td>
<td>1.55</td>
<td>-</td>
</tr>
<tr>
<td>0.100</td>
<td>0.375</td>
<td>1.85</td>
<td>-</td>
</tr>
<tr>
<td>0.100</td>
<td>0.250</td>
<td>1.20</td>
<td>-</td>
</tr>
</tbody>
</table>

\(\ast\) (OH\(^{-}\))\(_t\)'s were not determined in several runs.
**Fig. 5.** Rate of disappearance of hydroxide ion vs. borohydride concentration. Each curve at a constant ferricyanide concentration.

**Fig. 6.** Rate of disappearance of hydroxide ion vs. ferricyanide concentration. Each curve at a constant borohydride concentration.
For the lower curved end, however, the change of hydroxide ion concentration was not reproducible. It was thought that, for this part, the method of following the hydroxide ion concentration alone was not good enough for a kinetic study if a more complicated reaction was involved. Thus no further attempt has been made in this work to get exact information for this low hydroxide ion concentration region.

D. Surface Catalytic Effect in Low Concentration Region -- Check of Freund's Results

Since the surface catalytic effect was found to be important in this work, it should be worthwhile to check Freund's results for the reaction of ferricyanide with borohydride in low ferricyanide and borohydride concentration regions. In his experiments, solutions without stirring were contained in small glass cells used for absorption measurements. These cells had relatively large surface-volume ratios. A large surface catalytic effect, therefore, might be possible. To check this, results of two different runs with the same concentration were compared. One solution remained in the cell throughout the reaction (after Freund) and the other remained in a wax-coated beaker and was poured into the cell only when the absorption data were to be taken. The observation of no difference between the rates of the reaction under these two conditions implied that glass-surface catalytic effect was negligible in this low ferricyanide and borohydride concentration case.
Fig. 7 shows a typical result. However, two observations deviated from Freund's: (i) the rate constant differed from his value (Table 3); (ii) with initial ferricyanide ion concentration less than $10^{-4} \text{M}$, the rate of disappearance of ferricyanide ion began to slow down at a concentration which increased with decreasing initial ferricyanide ion concentration (Fig. 8).

<table>
<thead>
<tr>
<th>(Fe(CN)$_6^{3-}$) (M)</th>
<th>$-\frac{d(\text{Fe(CN)}_6^{3-})}{dt} \times 10^6$ (M min.$^{-1}$)</th>
<th>$k \times 10^{-8}$ (M$^{-1}$ min.$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$1 \times 10^{-3}$</td>
<td>7.7</td>
<td>2.2</td>
</tr>
<tr>
<td>$1 \times 10^{-4}$</td>
<td>6.7</td>
<td>1.9</td>
</tr>
<tr>
<td>$5 \times 10^{-5}$</td>
<td>6.4</td>
<td>1.8</td>
</tr>
</tbody>
</table>
| $1.5 \times 10^{-4}-18 \times 10^{-4}$ | 11.2                           | 3.2                             | This Work
|                        |                                 |                                 | Freund

Table 3. Experimental Values of $-\frac{d(\text{Fe(CN)}_6^{3-})}{dt}$ and $k$. ($\text{H}_2\text{O}$) = $3.5 \times 10^{-2}$ M, ($\text{OH}^-$) = $10^{-2}$ M, $t = 23^\circ$C.
Fig 7. $(\text{Fe(CN)}_6^{3-})$ vs time for two reactions with same concentration but different surfaces of containers.
$F_2 \cdot (\text{cm})^2 \cdot 10^{-5} \times (M)$

Fig. 9. $(F_2 \cdot (\text{cm})^2) = \text{vs. time with excess (BH}_4^- \text{) and (OH}^- \text{).}
III. RESULTS AND DISCUSSION

The discrepancy between Freund's rate equation and the preliminary observation in this laboratory for the reaction of ferricyanide with borohydride in alkaline aqueous solution with different concentration ranges has been affirmed. For the high ferricyanide and borohydride concentrations (both from 0.1 to 0.5M) case, experimental data gave the rate of the reaction as

\[-\frac{d(\text{OH}^-)}{dt} = k'(\text{BH}_4^-)(\text{Fe(CN)}_6^{3^-})\]  \hspace{1cm} (8)

at least for \((\text{OH}^-) > 7\times10^{-3}\text{M}\). The rate constant \(k'\) was measured to be \(4.93\times10^{-4}\text{ M}^{-1}\text{min}^{-1}\). The rate of disappearance of hydroxide ion should be equal to the rate of disappearance of ferricyanide ion according to the over-all stoichiometry (Eq. (5)). However, Eq. (8) was completely different from Eq. (6) as reported by Freund \((k = 3.2\times10^8\text{M}^{-1}\text{min}^{-1}\) at \(t = 23^\circ\text{C}\)).

It would be easier to understand if

\[k'(\text{BH}_4^-)(\text{Fe(CN)}_6^{3^-}) \gg k(\text{BH}_4^-)(\text{H}^+)\]  \hspace{1cm} (9)

for high \((\text{Fe(CN)}_6^{3^-})\)

and

\[k'(\text{BH}_4^-)(\text{Fe(CN)}_6^{3^-}) \ll k(\text{BH}_4^-)(\text{H}^+)\]  \hspace{1cm} (10)

for low \((\text{Fe(CN)}_6^{3^-})\)

then the \(k'(\text{BH}_4^-)(\text{Fe(CN)}_6^{3^-})\) term would be negligible in Freund's result while the \(k(\text{BH}_4^-)(\text{H}^+)\) term negligible in the result of this work. Unfortunately, even if relation (10) is true,
relation (9) does not hold. For example, with \((\text{BH}_4^-) = 0.2\text{M}, \,(\text{Fe(CN)}_6^{3-}) = 0.25\text{M}, (\text{OH}^-) = 10^{-2}\text{M} \text{ or } (\text{H}^+) = 10^{-12}\text{M}, k(\text{BH}_4^-)(\text{H}^+)\) was more than twice as large as \(k'(\text{BH}_4^-)(\text{Fe(CN)}_6^{3-})\). There is still no satisfactory explanation for these different rate laws. The main problem is that, even another mechanism led to the \(k'(\text{BH}_4^-)(\text{Fe(CN)}_6^{3-})\) term in the high concentration case, no one would expect the \(k(\text{BH}_4^-)(\text{H}^+)\) term to vanish as long as its value is of the same order as the \(k'(\text{BH}_4^-)(\text{Fe(CN)}_6^{3-})\) term.

The lower part of the hydroxide ion concentration vs. time plot is believed to arise from a more involved reaction. Below the turning point, which was at \((\text{OH}^-)_t = 5\times10^{-3} \text{ to } 7\times10^{-3}\text{M},\) the rate of disappearance of hydroxide ion became very fast and apparently depended on the concentration of hydroxide ion itself. However, it could not be reproduced. Other methods, which would be more effective than the pH measurement, should be used for further investigation.

The importance of surface catalysis in this reaction was an interesting discovery. This effect was positively proved to exist by the change of reaction rates in containers of different surfaces. It was found that wax-coated surface had the least catalytic effect. The reproducibility of results showed that surface catalysis was negligible for the reaction in a wax-coated beaker. Therefore, such beakers were used to obtain useful data. It would be instructive to point out here that the rate of reaction in a glass beaker was some ten times that
measured in a wax-coated one. Again, on the other hand, this glass-surface catalysis did not exist for low ferricyanide and borohydride case. Freund's result was thus checked to be independent of the surface of the container. However, a different rate constant and a deviation from zero order dependence of ferricyanide ion concentration of the rate law were observed.
ACKNOWLEDGMENTS

The author wishes to express her sincere appreciation for the inspiring guidance of Professor William L. Jolly whose advice, encouragement and unbounded interest provided a large contribution toward the completion of the work.

This work was performed under the auspices of the U.S. Atomic Energy Commission.
REFERENCES

This report was prepared as an account of Government sponsored work. Neither the United States, nor the Commission, nor any person acting on behalf of the Commission:

A. Makes any warranty or representation, expressed or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this report, or that the use of any information, apparatus, method, or process disclosed in this report may not infringe privately owned rights; or

B. Assumes any liabilities with respect to the use of, or for damages resulting from the use of any information, apparatus, method, or process disclosed in this report.

As used in the above, "person acting on behalf of the Commission" includes any employee or contractor of the Commission, or employee of such contractor, to the extent that such employee or contractor of the Commission, or employee of such contractor prepares, disseminates, or provides access to, any information pursuant to his employment or contract with the Commission, or his employment with such contractor.