*Inorganica Chimica Acta*, 29 (1978) 237–241
©Elsevier Sequoia S.A., Lausanne – Printed in Switzerland

# Oxidation of Thiols.
# III. Kinetics and Mechanism of Oxidation of Bis-1,5-diphenylformazan-3-yl Disulphide with Hexacyanoferrate(III) in Acid Medium

AHMAD Y. KASSIM
*Chemistry Department, Kuwait University, Kuwait*

Received December 10, 1977

---

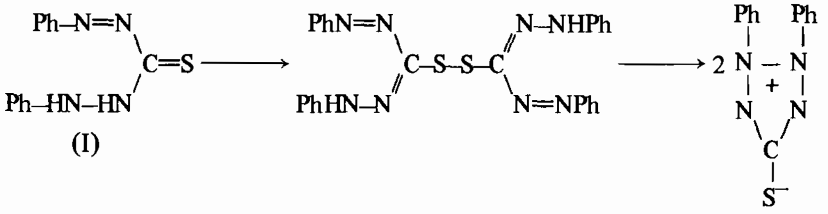
*The kinetics of oxidation of bis-1,5-diphenylformazan-3-yl disulphide(II) with hexacyanoferrate(III) showed a two term rate law with one path independent of* $[Fe(CN)_6^{3-}]$. *This last path which is acid independent in the pH range 1–6 is assumed to be due to the spontaneous decomposition of the disulphide(II) to diphenylthiocarbazone and 2,3-diphenyl-2H-tetrazolium-5-thiolate(III). The* $[Fe(CN)_6^{3-}]$ *dependent path is inversely dependent on* $[H^+]$ *in the pH range 5–6 but independent of* $[H^+]$ *in the pH range 1–2. The overall rate equation is*

$$Rate = (k_o + (k_2 + k_3/[H^+]))[Fe(CN)_6^{3-}]_T [RHSSHR]_T$$

*The activation energy and entropy for the spontaneous decomposition of the disulphide have the values* $E_a = 11.1$ *Kcal* $mol^{-1}$ *and* $\Delta S^* = -38.95 \pm 0.1$ *e.u. and for the* $[Fe(CN)_6^{-3}]$ *dependent path* $E_a = 14.58$ *Kcal* $mol^{-1}$ *and* $\Delta S^* = -23.2 \pm 0.15$ *e.u.*

## Introduction

1,5-diphenylthiocarbazone (dithizone) (I) is oxidized to bis-1,5-diphenylformazan-3-yl disulphide (II) with hexacyanoferrate(III). The kinetics and mechanism of this reaction in 50% ethanol–water mixture has been reported [1]. However, the disulphide (II) is further oxidized into the mesoionic dehydrodithizone, 2,3-diphenyl-2H-tetrazolium-5-thiolate (III) according to equation (i):



(i)

In this work the kinetics and mechanism of oxidation of (II) into (III) in the same solvent mixture are reported.

## Experimental

### *Chemicals*

All the chemicals used in this work were of ANALAR grade and were further purified as reported previously [1] to suit the dithizone procedures.

### *Glassware*

The glassware was carefully cleaned to remove any adsorbed metal ions on the glass surface. The glass surface after being treated with sulphuric–chromic acid mixture and then washed with distilled water was wetted with a solution of dithizone in chloroform. It was then washed with pure aliquots of chloroform and dried.

### *Instruments*

The pH measurements were carried out with a radiometer pH meter equipped with a combined glass electrode type GK 2311C. The pH meter readings were calibrated prior to use against radiometer buffers of pH's 4.01 ± 0.01 and 7.01 ± 0.01. The pH values in 50% ethanol–water mixture were converted into $[H^+]$ without being corrected. Kinetic measurements were carried out on a Unicam SP 700 spectrophotometer.

### *Procedure*

Due to the spontaneous decomposition of the disulphide (II) [2], its oxidation with $Fe(CN)_6^{3-}$ was followed after its rapid formation by the oxidation of dithizone. All the kinetic measurements were carried out under pseudo-first order conditions with hexacyanoferrate(III) in large excess (more than

TABLE I. Dependence of $k_{obs}$ on $[RHSSHR]_T$.[a]

| $[RHSSHR]_T \times 10^5$ | pH | $k_{obs} \times 10^3$ |
|---|---|---|
| 1.1 | 1.55 | 1.2 |
| 1.1 | 5.6 | 5.6 |
| 0.9 | 1.55 | 1.15 |
| 0.9 | 5.6 | 5.5 |
| 0.75 | 1.55 | 1.15 |
| 0.75 | 5.6 | 5.4 |
| 0.5 | 1.55 | 1.23 |

[a] $I = 0.2\ M$; $[Fe(CN)_6^{3-}]_T = 0.75 \times 10^{-3}$; Temp = 25 °C.

tenfold). The ethanolic solution of dithizone was placed in one side of an indented flask and in the other, the buffer (HCl–sodium acetate mixture) and hexacyanoferrate(III) were added. The flask after being thermostated for at least 20 minutes was well shaken to mix the two solutions and an aliquot was taken and placed in a 1 cm quartz cell which was kept in the thermostated cell holder of the spectrophotometer. The decrease in absorbance as a function of time was monitored at 420 nm. The pH of each reaction mixture was then recorded.

## Results

### *Identification of the Products and Stoichiometry of the Reaction*

Dithizone is characterized by the presence of two widely separated bands in its visible absorption spectrum (*e.g.*, 590 nm and 428 nm in 50% ethanol–water mixture) [3, 4]. However, all its known oxidation products do not absorb in the region around 600 nm [5]. This fact aided in the prediction of the mechanism of both its oxidation to the disulphide(II)

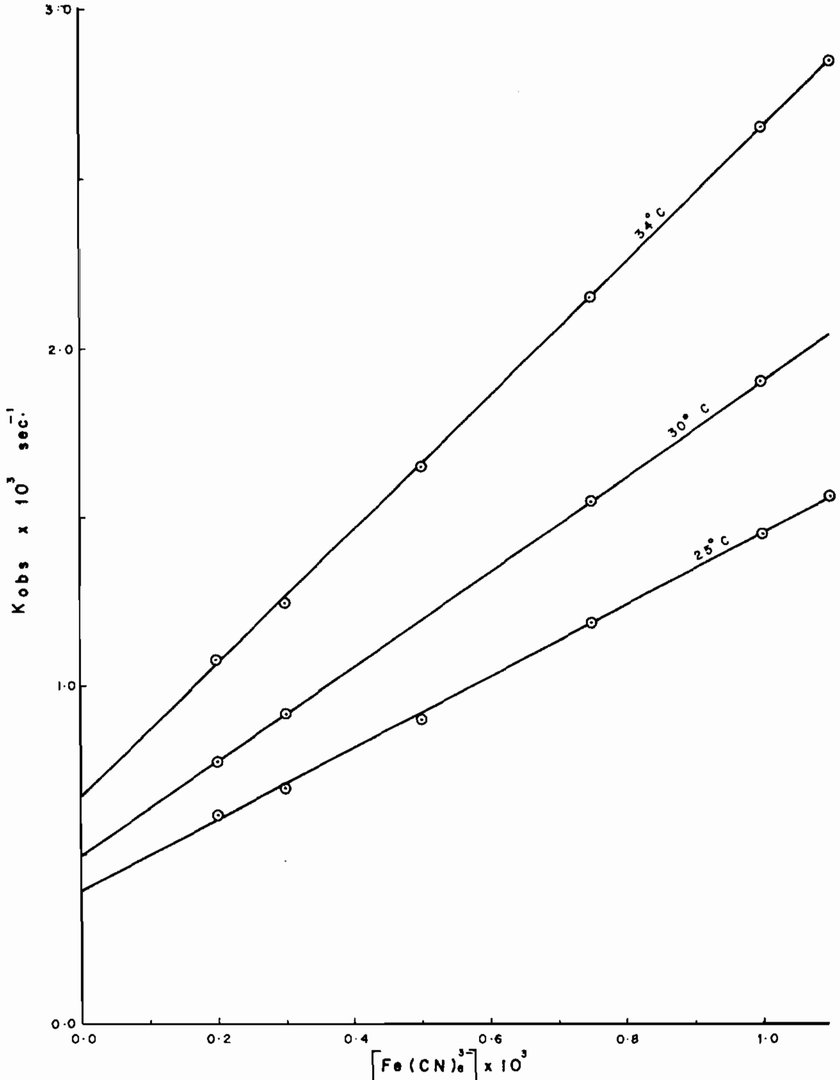


Figure 1. Plot of $k_{obs}$ *vs.* $[Fe(CN)_6^{3-}]$ at various temperatures. $I = 0.2\ M$, $[RHSSHR]_T = 1.25 \times 10^{-5}\ M$, pH = 1.55.

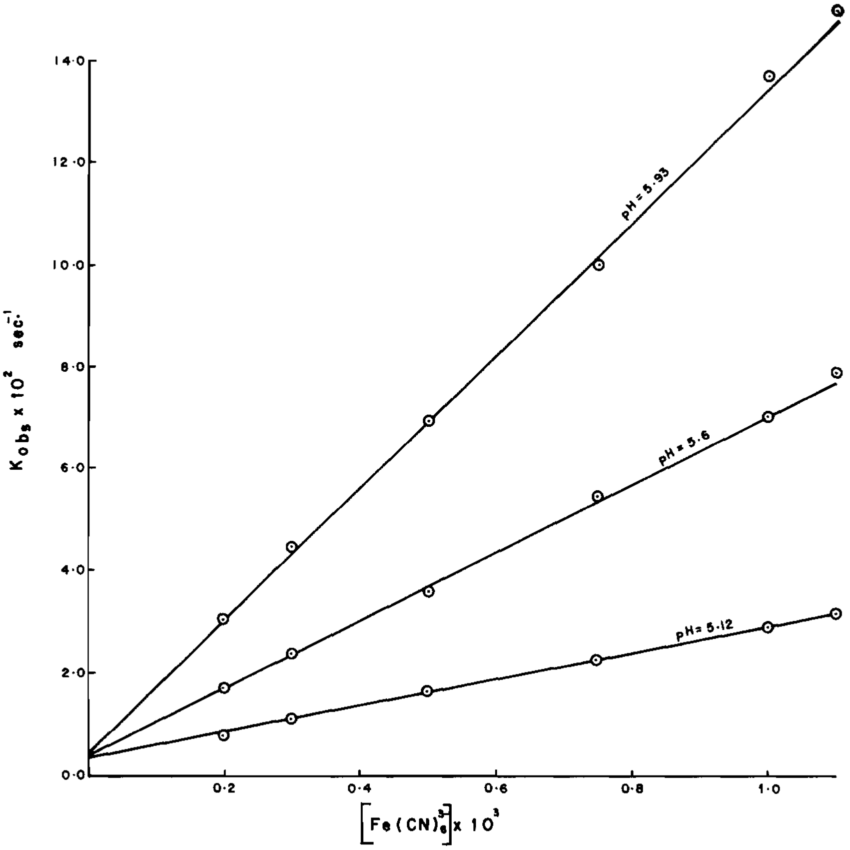


Figure 2. Variation of $k_{obs}$ with $[Fe(CN)_6^{3-}]$ at different pH values. Temp. = 25 °C, I = 0.2 *M*, $[RHSSHR]_T = 1.25 \times 10^{-5}$ *M*.

and the oxidation of (II) into the mesoionic compound (III). At 420 nm, the oxidation of dithizone results in an increase of absorbance as a consequence of the high molar absorptivity of the disulphide (II) (50,000) [1]. The oxidation of the disulphide (II) to the mesoionic compound (III) ($\epsilon_{416}$ = 1150) was studied (the stoichiometry represented by eqn. i has been reported [1] in the pH ranges 1–2 and 5–6 by following the decrease in absorbance at 420 nm). In both ranges the formation of the disulphide (II) is much faster than its oxidation to compound (III). In the pH range 2–3, it was difficult to study the oxidation of the disulphide (II) as the rates of its oxidation are not too different from those of its formation (the oxidation of (I) decreases with $[H^+]$ and then increases).

### *Kinetics*

With $[Fe(CN)_6^{3-}]$ in excess ($2 \times 10^{-4}$–$1.25 \times 10^{-3}$ *M*) of that of the disulphide (II) the plots of log($A_t - A_\infty$) (where $A_t$ and $A_\infty$ are the absorbances at time t and at infinity respectively) *vs.* time gave straight lines up to around 80% of the reaction (the first few points were neglected). Table I gives the values of the pseudo-first order rate constants ($k_{obs}$, $sec^{-1}$) over the range in which the concentration of the disulphide(II) was varied.

TABLE II. Dependence of $k_{obs}$ on $[H^+]$ in the pH Range 1–2.[a]

| pH | $k_{obs} \times 10^4$ |
|---|---|
| 1.2 | 9.1 |
| 1.37 | 9.23 |
| 1.57 | 8.9 |
| 1.63 | 8.8 |
| 1.9 | 9.1 |

[a] $[RHSSHR]_T = 1.25 \times 10^{-5}$; $[Fe(CN)_6^{3-}]_T = 0.5 \times 10^{-3}$; I = 0.2 *M*; Temp. = 25 °C.

Figs. 1 and 2 show that $k_{obs}$ varies linearly with $[Fe(CN)_6^{3-}]$ at all pH values and the dependence agrees with eqn. 1

$$k_{obs} = k_o + k_1[Fe(CN)_6^{3-}]_T \quad (1)$$

where $k_o$ corresponds to the intercept and $k_1$ is the slope. From Table II, $k_o$ and $k_1$ are acid independent in the pH range 1–2 and have the values $4 \times 10^{-4}$ $sec^{-1}$ and 1.05 $sec^{-1}$ $M^{-1}$ at 25 °C. Hence, the rate equation in the pH range 1–2 is represented by eqn. 2.

$$Rate = (k_o + k_1[Fe(CN)_6^{3-}]_T)[RHSSHR]_T \quad (2)$$

However, in the pH range 5–6, a plot of $k_{obs}$ against $[Fe(CN)_6^{3-}]$ (Fig. 2) shows that $k_1$ varies inversely with $[H^+]$ and the dependence is described by eqn. 3

$$k_1 = k_2 + k_3/[H^+] \tag{3}$$

where $k_2$ = 1.00 $sec^{-1}$ $M^{-1}$, which is comparable to the value of $k_1$ in the pH range 1–2 and $k_3$ = 1.52 × $10^{-4}$ $sec^{-1}$ $M^{-2}$ at 25 °C. Hence, the overall rate equation in the pH range 5–6 is described by eqn. 4.

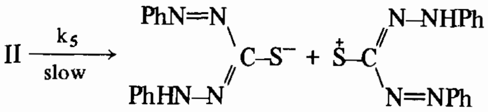
$$\text{Rate} = \{k_o + (k_2 + (k_3/[H^+])[Fe(CN)_6^{3-}]_T\} [RHSSHR]_T \tag{4}$$

Eqn. 4 reduces to eqn. 2 if the factor $k_3/[H^+]$ is neglected at low acid concentrations.

A plot of $\log k_o$ *vs.* 1/T yielded $E_a$ = 11.1 Kcal $mol^{-1}$ and $\Delta S^*$ = −38.95 ± 0.1 e.u. for the spontaneous decomposition of (II), and a plot of $\log k_1$ against 1/T yielded $E_a$ = 14.58 Kcal $mol^{-1}$ and $\Delta S^*$ = −23.2 ± 0.15 e.u. for the $[Fe(CN)_6^{3-}]$ dependent path.

## Discussion

The kinetics of oxidation of the disulphide (II) (referred to as RHSSHR, where the two protons are attached to nitrogen atoms) showed a two term rate law with one path independent of the concentration of $Fe(CN)_6^{3-}$. This last path is consistent with reaction 5 being rate determining.


(5)

IV (denoted later as $RH\bar{S}$)

V (denoted as $RH\overset{+}{S}$)

$$RHS^{+} \longrightarrow RS + H^{+} \tag{6}$$

$$RS \longrightarrow III \tag{7}$$

$$RHS^{-} + Fe(CN)_6 \xrightarrow{\text{fast}} RHS^{\bullet} \tag{8}$$

$$2RHS^{\bullet} \xrightarrow{\text{fast}} RHSSHR \tag{9}$$

The spontaneous decomposition of (II) into (IV) and (V) and their consequent oxidation to (I) and (III) respectively was reported [2]. Later, it was also confirmed that other analogues of the disulphide (II), namely, bis-1,5-di(2-fluorophenyl)formazan-3-yl disulphide and bis-1,5-di(2-methylphenyl)formazan-3-yl disulphide undergo such spontaneous fission of the sulphur–sulphur bond to give the corresponding analogue of the mesoionic compound (III) [6]. The heterolytic fission shown in equation 3 was assumed [2] on the basis of e.s.r. measurements which failed to detect free radicals characteristic of a homolytic cleavage, and the effect of the polarity of the solvent on the reaction rate. The oxidation of the anion (IV) to RHSSHR is known to be very fast [1]. Both Fig. 2 and Table I show that reaction 3 is acid independent in the pH range 1–6. This is not unlikely because the spontaneous decomposition of the disulphide (II) is a function of the polarity of the solvent. To mention, the polarity of water (Z, Kosower's solvent polarity parameter = 94.6) does not differ markedly from that of 1*M* HCl (Z = 96.6) [7].

The $[Fe(CN)_6^{3-}]$ dependent path is catalysed by the decrease in $[H^+]$ in the pH range 5–6 (Fig. 2). This is, perhaps due to release of an imino proton from the disulphide (II). This process is not unexpected. Thus, although the $pK_2$ of dithizone (I) is considered to be greater than 14 [8], the imino proton is known to be easily released from its copper, silver and mercury complexes [8–10].

The data in Table II show that the protonated forms of $Fe(CN)_6^{3-}$ which are known [1] to catalyse the oxidation of dithizone by the formation of hydrogen bonds with the sulphur atom of its thione form, are not effective in the oxidation of the disulphide (II) in the same pH range [1–2].

On the basis of the above discussion, the following reactions may be proposed for the oxidation of the disulphide(II) with $Fe(CN)_6^{3-}$

$$RHSSHR \underset{}{\overset{K}{\rightleftharpoons}} RHSSR^{-} + H^{+} \tag{10}$$

$$RHSSHR + Fe(CN)_6^{3-} \xrightarrow{k_{11}} RHSSHR^{+} + Fe(CN)_6^{4-} \tag{11}$$

$$RHSSR^{-} + Fe(CN)_6^{3-} \xrightarrow{k_{12}} RHSSR^{\bullet} \tag{12}$$

$$RHSSHR^{+} \longrightarrow RHS^{+} + RHS \tag{13}$$

$$RHSSR^{\bullet} \longrightarrow RHS^{+} + RS \tag{14}$$

$$RHS^{+} \longrightarrow RS + H^{+} \tag{15}$$

$$2RHS \longrightarrow RHSSHR \tag{16}$$

$$RS \longrightarrow \text{Meso} \tag{17}$$

Due to low concentrations of $HFe(CN)_6^{2-}$ and $H_2Fe(CN)_6^{-}$ in the pH range studied, their role may be neglected.

From equations 5, 10, 11, and 12:

$$\text{Rate} = k_5[RHSSHR] + k_{11}[RHSSHR][Fe(CN)_6^{3-}]_T + k_{12}[RHSSR^{-}][Fe(CN)_6^{3-}]$$

$$[\mathrm{RHSSR^-}] = \frac{K[\mathrm{RHSSHR}]_T}{[\mathrm{H^+}] + K}$$

$$[\mathrm{RHSSHR}] = \frac{[\mathrm{H^+}]\,[\mathrm{RHSSHR}]_T}{[\mathrm{H^+}] + K}$$

Hence,

$$\mathrm{Rate} = \frac{k_5[\mathrm{RHSSHR}]_T[\mathrm{H^+}]}{[\mathrm{H^+}] + K} + \frac{[\mathrm{RHSSHR}]_T[\mathrm{Fe(CN)_6}]_T}{[\mathrm{H^+}] + K}(k_{11}[\mathrm{H^+}] + k_{12}K) \qquad (19)$$

If K is neglected in comparison to $[\mathrm{H^+}]$ in the pH range studied, then eqn. 19 reduces to eqn. 20:

$$\mathrm{Rate} = k_5[\mathrm{RHSSHR}]_T + k_{11}[\mathrm{RHSSHR}]_T[\mathrm{Fe(CN)_6^{3-}}]_T + \frac{k_{12}K[\mathrm{RHSSHR}]_T[\mathrm{Fe(CN)_6^{3-}}]_T}{[\mathrm{H^+}]} \qquad (20)$$

which is equivalent to equation 4, where $k_5 = k_o$, $k_{11} = k_2 = 1.0\ \mathrm{sec^{-1}}\ M^{-1}$ and $k_{12}K = k_3 = 1.52 \times 10^{-4}\ \mathrm{sec^{-1}}\ M^{-2}$ at 25 °C.

In the pH range 1–2, the term

$$\frac{k_{12}K[\mathrm{RHSSHR}]_T[\mathrm{Fe(CN)_6^{3-}}]_T}{[\mathrm{H^+}]}$$

may be neglected and equation 21 is obtained:

$$\mathrm{Rate} = k_5[\mathrm{RHSSHR}]_T + k_{11}[\mathrm{RHSSHR}]_T[\mathrm{Fe(CN)_6^{3-}}]_T \qquad (21)$$

which is equivalent to equation 2, where $k_5 = k_o$ and $k_{11} = k_1$.

## References

1 A. Y. Kassim, *Inorg. Chim. Acta, 27,* 243 (1978).
2 A. M. Kiwan and H. M. N. H. Irving, *J. Chem. Soc. B,* 901 (1971).
3 E. B. Sandell, "Colorimetric Determination of Traces of Metals", 2nd edn., Interscience, New York (1959).
4 G. Iwantscheff, "Das Dithizon und Seine Anwendung in der Mikro- und Spurenanalyse", Verlag Chemie, Weinheim (1972).
5 H. M. N. H. Irving, A. M. Kiwan, D. C. Rupainwar and S. S. Sahota, *Anal. Chim. Acta, 26,* 205 (1971).
6 A. Y. Kassim, Unpublished Work.
7 E. M. Kosower, *J. Am. Chem. Soc., 80,* 3253 (1958).
8 R. W. Geiger and E. B. Sandell, *Anal. Chim. Acta, 8,* 197 (1953).
9 L. S. Meriwether, E. C. Breitner and N. B. Colthup, *J. Am. Chem. Soc., 87,* 448 (1965).
10 G. B. Briscoe and S. Humphries, *Talanta, 18,* 39 (1971).