September, 1979] BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 52 (9), 2535—2539 (1979) 2535

# Kinetics of the Reduction Reaction of Tetranitromethane by Thiosulfate Ion in the Absence and Presence of Copper(II) Ion in Aqueous Mixtures of Methanol and Ethanol

Masaru KIMURA* and Makiko SHUKUTANI
*Department of Chemistry, Faculty of Science, Nara Women's University, Nara 630*

(Received December 4, 1978)

The kinetics of the reduction reaction of tetranitromethane by the thiosulfate ion in the absence and presence of the copper(II) ion have been investigated in aqueous solution and aqueous mixtures of methanol and ethanol. The mechanism of reaction has been thought to be the following:

$$C(NO_2)_4 + S_2O_3^{2-} \xrightarrow{k_1} C(NO_2)_3^- + NO_2 + S_2O_3^-$$

$$Cu(II) + S_2O_3^{2-} \xrightarrow{k_2} Cu(I) + S_2O_3^-$$

$$C(NO_2)_4 + Cu(I) \xrightarrow{k_3} C(NO_2)_3^- + NO_2 + Cu(II)$$

$$2S_2O_3^- \xrightarrow{\text{rapid}} S_4O_6^{2-}$$

The rate constants $k_1$ and $k_2$ have been determined under several conditions. The value of $k_1$ was hardly affected by ionic strength, permittivity, and acetate ion concentration in the reaction solution, whereas $k_2$ was markedly increased with decreasing ionic strength ($\mu$), permittivity ($D$), and acetate ion concentration. For $k_2$, plots of $\log k_2$ *vs.* $\mu^{1/2}/(1+\mu^{1/2})$ and $\log k_2$ *vs.* $1/D$ gave linear relationships. Under the specified conditions the $k_2$-term in the reaction mechanism accounts for up to 90% of the reaction, the reaction being composed of a copper(II) catalyzed-chain reaction.

Tetranitromethane (TNM) is reduced by solvated electrons and other reducing radicals such as $H^{\cdot}$, $O_2^{\cdot-}$, $CO_2^{\cdot-}$, $\dot{C}H_2OH$, and so forth,[1-7] becoming the nitroform anion ($NF^-$) which has a strong absorption peak at 350 nm. Most studies on the TNM reduction reaction have been made by pulse radiolysis techniques, and thus the reducing substances have been restricted to the radical species. The reduction reaction of TNM by reducing agents such as thiosulfate has received little investigation.

Recently, Sellers and Simic[2] and Asmus *et al.*[7] reported that tetranitromethane is easily reduced to the nitroform anion by the copper(I) ion. It is known that the copper(II) ion undergoes facile reduction to the copper(I) ion by the thiosulfate ion in aqueous solution. Thus, it is assumed that tetranitromethane would be reduced by the copper(I) ion which is produced by the reaction between the copper(II) ion and thiosulfate ion. The present paper reports the TNM reduction reaction induced by the reaction between the copper(II) ion and the thiosulfate ion. The large molar absorptivity of the nitroform ion permits low concentrations of the reactants to be used, thus reducing or eliminating problems from the limited solubility of the tetranitromethane and complexing side reactions related to the thiosulfate reaction. The concentrations used were $1\times10^{-5}$—$3\times10^{-4}$ mol dm$^{-3}$ in TNM, $5\times10^{-4}$—$5\times10^{-3}$ mol dm$^{-3}$ in sodium thiosulfate, and $0$—$2\times10^{-4}$ mol dm$^{-3}$ in copper(II) sulfate.

## Experimental

*Chemicals.* Sodium perchlorate used for adjusting the ionic strength was recrystallized twice from aqueous solution. Methanol and ethanol were distilled in a glass still. Deionized water was further distilled through permanganate solution in a glass still. All other chemicals used were of analytical reagent grade.

*Procedure and Apparatus.* Unless otherwise stated the reaction of tetranitromethane with thiosulfate ion in the presence of the copper(II) ion was initiated by the addition of thiosulfate solution into the mixture of tetranitromethane and copper(II) under the conditions given. The nitroform anion which is the reduction product of tetranitromethane has an extremely large absorptivity $\varepsilon=1.5\times10^4$ dm$^3$ mol$^{-1}$ cm$^{-1}$ at 350 nm,[8] and the other species in the reaction solution are transparent under the given concentrations. Consequently the absorbance of the nitroform anion ($NF^-$) formed was measured at appropriate time of reaction using a Hitachi Model 100-40 spectrophotometer. The cell housing was thermostatted at constant temperature, and in the dark except for the time measuring absorbance.

## Results and Discussion

*In the Absence of Copper(II).* Tetranitromethane was slowly reduced by thiosulfate ion. The reduction rate may be described by Eq. 1.

$$-d[TNM]/dt = d[NF^-]/dt = k_1[TNM][S_2O_3^{2-}] \qquad (1)$$

With excess thiosulfate, Eq. 2 is deduced:

$$\ln(A_\infty - A_t)/A_\infty = -k_{\text{obsd}}t \qquad (2)$$

where $k_{\text{obsd}}=k_1[S_2O_3^{2-}]$; $A_\infty$ and $A_t$ indicate the absorbance of $NF^-$ formed at infinity and time $t$, respectively. A plot of the left-hand side of Eq. 2 against time gave a linear relationship over three half-lives, and the value of $A_\infty$ was proportional to the amount of tetranitromethane added initially. An example of the plots according to Eq. 2 is given in Fig. 1. All the rate constants $k_1$ obtained are tabulated in Tables 1 and 2, and given in Figs. 4 and 5 together with the rate constant $k_2$ in the presence of copper(II) (*vide infra*).

*Reaction in the Presence of Copper(II).* The reduction rate of tetranitromethane by thiosulfate ion was greatly accelerated by the addition of small amounts of copper(II) ion. The rate did not obey Eq. 2. The plots of $A_t$ against reaction time showed a linear

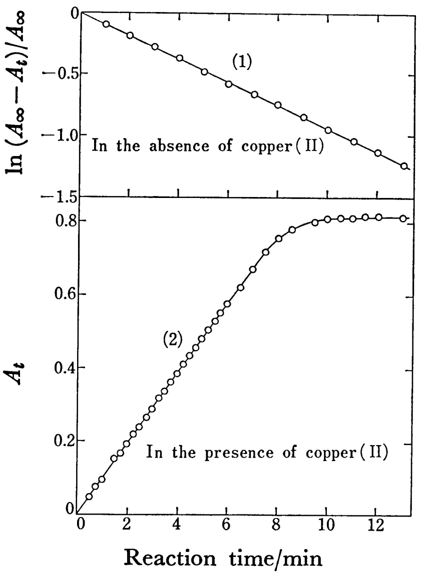

Fig. 1. Examples of the kinetic run in the absence and presence of copper(II) ion. $4.0\times10^{-3}$ mol dm$^{-3}$ in sodium thiosulfate and $5.4\times10^{-5}$ mol dm$^{-3}$ tetranitromethane for line 1; $1.0\times10^{-3}$ mol dm$^{-3}$ in sodium thiosulfate, $5.4\times10^{-5}$ mol dm$^{-3}$ tetranitromethane, and $5.0\times10^{-5}$ mol dm$^{-3}$ in copper(II) sulfate for curve 2; 25 °C; the other conditions as in Table 2.

relationship over half-life time of reaction, indicating the reaction to be of zero order with respect to the TNM concentration. An example of the kinetic behavior is illustrated in Fig. 1 together with the plot according to Eq. 2 in the absence of copper(II) ion. The initial rate of the reaction in the presence of copper(II) ion $V_I$=d[NF$^-$]/d$t$, was evaluated from the initial slope of the plot of $A_t$ *vs.* $t$.

*Dependence of the Reaction Rate on TNM Concentration.* The dependence of the reaction rate on the tetranitromethane concentration was examined at zero, $5.0\times10^{-5}$, and $2.0\times10^{-4}$ mol dm$^{-3}$ in copper(II) sulfate and is illustrated in Fig. 2. With a concentration of [TNM]$\geq$[Cu(II)], the slopes in the plots became equal to each other irrespective of the copper(II) ion concentrations, and the values of the intercept extrapolated to zero TNM increased with increasing copper(II) concentration.

*Dependence of the Reaction Rate on Concentration of Copper(II) and Thiosulfate.* Plots of $V_I$ against copper(II) concentration showed linear relationships, and both the intercepts and slopes were found directly proportional to the thiosulfate concentration. Some examples of the plots are given in Fig. 3. The rate constant $k_2$ was evaluated from the slope of the plot of $V_I$ *vs.* [Cu(II)].

*Reaction Mechanism.* All the results obtained are accounted for by Reactions 3—6, and the rate law (7).

$$C(NO_2)_4 + S_2O_3^{2-} \xrightarrow{k_1} C(NO_2)_3^- + NO_2 + S_2O_3^- \quad (3)$$

$$Cu(II) + S_2O_3^{2-} \xrightarrow{k_2} Cu(I) + S_2O_3^- \quad (4)$$

$$C(NO_2)_4 + Cu(I) \xrightarrow{k_3} C(NO_2)_3^- + Cu(II) + NO_2 \quad (5)$$

$$2S_2O_3^- \xrightarrow{\text{rapid}} S_4O_6^{2-} \quad (6)$$

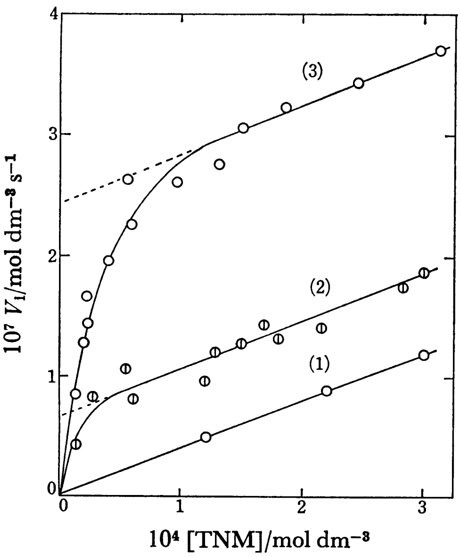

Fig. 2. Dependence of initial rate on the tetranitromethane concentration. Zero, $5.0\times10^{-5}$, and$2.0\times10^{-4}$ mol dm$^{-3}$ in copper(II) sulfate for curves 1, 2, and 3, respectively; varied concentrations of tetranitromethane; 25 °C; the other conditions as in Table 2.

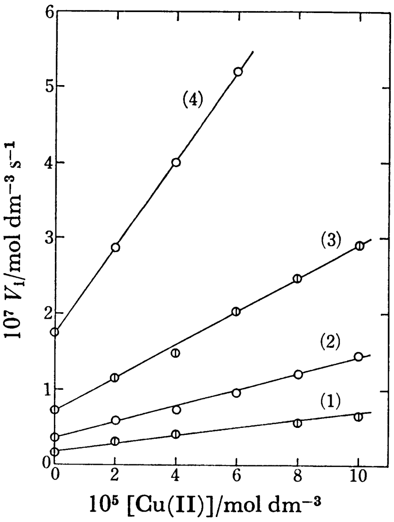

Fig. 3. Dependence of initial rate on concentrations of copper(II) and thiosulfate ions. $5.0\times10^{-4}$, $1.0\times10^{-3}$, $2.0\times10^{-3}$, and $5.0\times10^{-3}$ mol dm$^{-3}$ in sodium thiosulfate for lines 1, 2, 3, and 4, respectively; 20 °C; varied concentrations of copper(II) sulfate; the other conditions as in Table 2.

Under the conditions of $k_3[C(NO_2)_4][Cu(I)] \gg k_2[Cu(II)][S_2O_3^{2-}]$, the rate of formation of the nitroform anion is described by Eq. 7.

$$V_I = d[NF^-]/dt = k_1[TNM][S_2O_3^{2-}] + k_2[Cu(II)][S_2O_3^{2-}] \quad (7)$$

Under the condition of the $k_2$-term in Eq. 7 being much larger than the $k_1$-term, the rate shows zero-order with respect to the TNM concentration. Reactions 4 and 5 as alternative mechanisms could be also represented by Reactions 4′ and 5′.

$$\mathrm{Cu(II)} + \mathrm{S_2O_3}^{2-} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} \mathrm{Cu(II)\cdot S_2O_3}^{2-} \qquad (4')$$

$$\mathrm{C(NO_2)_4} + \mathrm{Cu(II)\cdot S_2O_3}^{2-} \xrightarrow{k_3} \mathrm{C(NO_2)_3}^- + \mathrm{Cu(II)} + \mathrm{S_2O_3}^- + \mathrm{NO_2} \qquad (5')$$

Assuming the steady concentration for $\mathrm{Cu(II)\cdot S_2O_3}^{2-}$ under the conditions of $k_3[\mathrm{TNM}] \gg k_{-2}$, an equation identical to Eq. 7 is formed.

*Ionic Strength Dependence on $k_1$ and $k_2$.* Although the values of $k_1$ were independent of the ionic strength of the reacting solution, the values of $k_2$ decreased with increasing the ionic strength. Plots of the extended Debye-Hückel equation are given in Fig. 4. The value of the slope of log $k_2$ *vs.* $\mu^{1/2}/(1+\mu^{1/2})$ was $-1.53$ a value somewhat smaller than the absolute value predicted for the reaction between divalent ions.

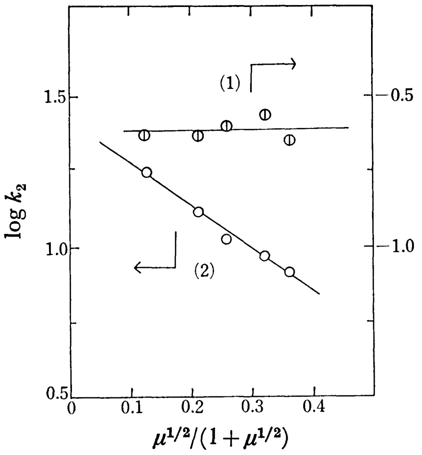

Fig. 4. Ionic strength effects on the rate constants. 0.01 mol dm$^{-3}$ in perchloric acid ; 0.02 mol dm$^{-3}$ in sodium acetate; 20 °C; varied ionic strengths ($\mathrm{NaClO_4}$); the other condtions as in Table 1.

This may indicate that the copper(II) ion exists as acetato complexes so that the effective charges reveal smaller values than the divalent ion. Using the data, $K_1 = 1\times10^2$ dm$^3$ mol$^{-1}$ and $\beta_2 = 1\times10^3$ dm$^6$ mol$^{-2}$ for the formation constants of acetato- and diacetato-copper(II) complexes, respectively,[9] in a solution of $1\times10^{-4}$ mol dm$^{-3}$ copper(II) and 0.01 mol dm$^{-3}$ acetate ion the copper(II) exists as $4.8\times10^{-5}$ mol dm$^{-3}$ $\mathrm{Cu_{aq}}^{2+}$ + $4.8\times10^{-5}$ mol dm$^{-3}$ $\mathrm{CuOAc}^+$ + $4\times10^{-6}$ mol dm$^{-3}$ $\mathrm{Cu(OAc)_2}$ in aqueous solution. Therefore, approximately 50% of copper(II) exists as $\mathrm{CuOAc}^+$ species.

*Permittivity Dependence of $k_1$ and $k_2$.* The addition of methanol and ethanol to the reaction solution remarkably accelerated the rate of reaction between tetranitromethane and thiosulfate ion in the presence of the copper(II) ion. Plots of log $k_1$ *vs.* $1/D$ and log $k_2$ *vs.* $1/D$ are given in Fig. 5.

Assuming $Z_aZ_b = -4$ for the $k_2$ reaction, the distance of the closest approach of the reactants in the transition state has been calculated to be $3\times10^{-8}$ cm. The dependence of $k_1$ on the permittivity was much smaller than for $k_2$. The dependence of $k_1$ may indicate that the tetranitromethane molecule is polarized in the transition state, and that side reactions may occur with increasing alcohol concentration.

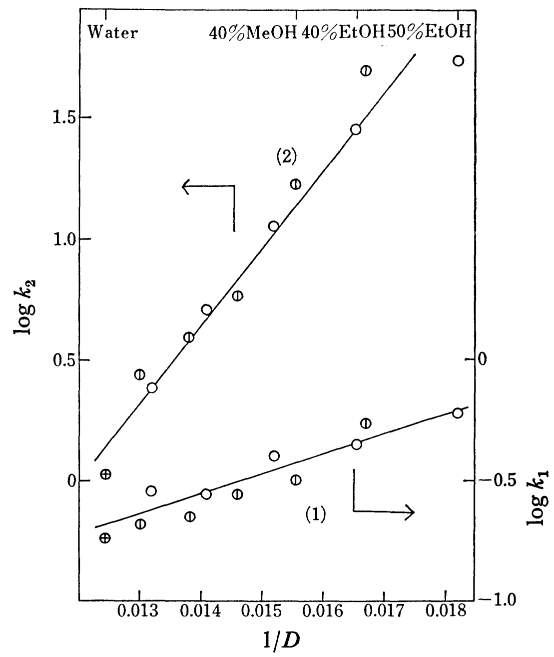

Fig. 5. Permittivity dependence on the rate constants. Plots ⊕, ⦶, and ○ indicate the data in aqueous solution, those in aqueous mixtures with methanol, and those in aqueous mixtures with ethanol, respectively. Varied concentrations 0, $5.0\times10^{-6}$, $1.0\times10^{-5}$, $2.0\times10^{-5}$, $3.0\times10^{-5}$, $4.0\times10^{-5}$, and $5.0\times10^{-5}$ mol dm$^{-3}$ in copper(II) sulfate for the aqueous mixtures with methanol and ethanol; 0, $2.0\times10^{-5}$, $5.0\times10^{-5}$, $1.0\times10^{-4}$, and $1.5\times10^{-4}$ mol dm$^{-3}$ in copper(II) sulfate for the aqueous solution; 20 °C; the other conditions as in Table 2. Values of permittivity were cited from a literature by Åkerlöf.[14]

*Effect of Acetate Ion.* The rate constant $k_1$ was not affected by the acetate ion concentration, whereas $k_2$ remarkably decreased with increasing acetate ion concentration. This strong retardation may be due to complex formation of the copper(II) ion with the acetate ion. Assuming that the aquated copper(II) ion is the main reacting species, $k_2$ should be described by Eq. 8.

$$k_2 = k_2^\circ/(1+K_1[\mathrm{OAc}^-] + \beta_2[\mathrm{OAc}^-]^2) \qquad (8)$$

where $k_2^\circ$ indicates $k_2$ in the absence of acetate ion. Using values of $k_2^\circ = 20$ dm$^3$ mol$^{-1}$ s$^{-1}$, $K_1 = 1\times10^2$ dm$^3$ mol$^{-1}$, and $\beta_2 = 1\times10^3$ dm$^6$ mol$^{-2}$, $k_2$ has been calculated to be 20, 9.5, 5.9, 3.0, 1.9, and 1.0 dm$^3$ mol$^{-1}$ s$^{-1}$ for zero, 0.01, 0.02, 0.04, 0.06, and 0.10 mol dm$^{-3}$ concentrations of $\mathrm{OAc}^-$, respectively. The values calculated are in good agreement with those obtained experimentally. The rate constants $k_1$ and $k_2$ obtained are tabulated in Table 1.

*Temperature Dependence.* The values of $k_1$ and $k_2$ were determined in aqueous solution at an ionic strength of 0.2 mol dm$^{-3}$ containing 0.1 mol dm$^{-3}$ acetate ion at 15, 20, 25, 30, and 35 °C the results of which are listed in Table 2. The values of $k_1$ and $k_2$ are described by:

$$k_1 = 1.4\times10^9 \exp[-54000\,\mathrm{J\,mol^{-1}}/RT]\ \mathrm{dm^3\,mol^{-1}\,s^{-1}}$$

and

Table 1. Acetate ion effect on the $k_1$ and $k_2$[a)]

| $[CH_3COO^-]$/mol dm$^{-3}$ | $k_1$/dm$^3$ mol$^{-1}$ s$^{-1}$ | $k_2$/dm$^3$ mol$^{-1}$ s$^{-1}$ |
|---|---|---|
| 0[b)] | 0.239[b)] | 20.0[b)] |
| 0.01 | 0.266 | 9.53 |
| 0.02 | 0.266 | 8.62 |
| 0.04 | 0.256 | 5.59 |
| 0.06 | 0.202 | 1.61 |
| 0.10 | 0.187 | 1.06 |

a) $1.5\times10^{-4}$ mol dm$^{-3}$ tetranitromethane; $1.0\times10^{-3}$ mol dm$^{-3}$ sodium thiosulfate; 0, $2.0\times10^{-5}$, $5.0\times10^{-5}$, $1.0\times10^{-4}$, and $1.5\times10^{-4}$ mol dm$^{-3}$ in copper(II) sulfate; varied concentrations of sodium acetate and perchloric acid maintaining the ratio 2 : 1 and pH 4.7 at 20 °C; ionic strength 0.2 mol dm$^{-3}$ ($NaClO_4$). b) pH 5.0 at the unbuffered solution; other conditions as in a).

Table 2. Temperature dependence on the rate constants[a)]

| Temp/°C | $k_1$/dm$^3$ mol$^{-1}$ s$^{-1}$ | $k_2$/dm$^3$ mol$^{-1}$ s$^{-1}$ |
|---|---|---|
| 15 | 0.158 | 0.82 |
| 20 | 0.187 | 1.06 |
| 25 | 0.394 | 1.23 |
| 30 | 0.556 | 1.66 |
| 35 | 0.680 | 2.00 |

a) Conditions as in Table 1; except 0.1 mol dm$^{-3}$ in perchloric acid and 0.2 mol dm$^{-3}$ in sodium acetate, and varied temperatures.

$$k_2 = 1.1\times10^6 \exp[-33000\,\mathrm{J\,mol^{-1}}/RT]\ \mathrm{dm^3\,mol^{-1}\,s^{-1}},$$

respectively.

*Mixing Order of Reactants.* The addition of the copper(II) ion to the thiosulfate solution before the addition of tetranitromethane results in the formation of copper(I) in solution and the concentration of the copper(I) increases with standing of the copper(II)–thiosulfate mixture. The addition of tetranitromethane to the mixture after a certain time of standing resulted in the tetranitromethane reacting rapidly with all the copper(I) produced during the standing time resulting in the nitroform ion. After the rapid formation of nitroform ion, the nitroform ion concentration increased with time. An example of the behavior is given in Fig. 6.

The values extrapolated to zero time in Fig. 6 correspond to the concentrations of copper(I) formed during the standing time. The extrapolated values, plotted against the standing time of the copper(II)–thiosulfate mixture are given in Fig. 7 together with the results obtained under different conditions.

The slopes in Fig. 7 at zero to about ten min correspond to the rate of reaction between copper(II) and thiosulfate, and increases with decreasing acetate ion concentration. This trend is the same as seen in the values of $k_2$ in Table 1. From the initial slopes in Fig. 7 $k_2$ has been evaluated approximately as 4 to 6 dm$^3$ mol$^{-1}$ s$^{-1}$ and 1 dm$^3$ mol$^{-1}$ s$^{-1}$ in 0.01 and 0.1 mol dm$^{-3}$ acetate ion, respectively. It is seen from Fig. 7 that the amount of nitroform formed is not related to the molecular oxygen dissolved in solution. Fouda *et al.*[10,11)] reported that at temperatures up to 50 °C and

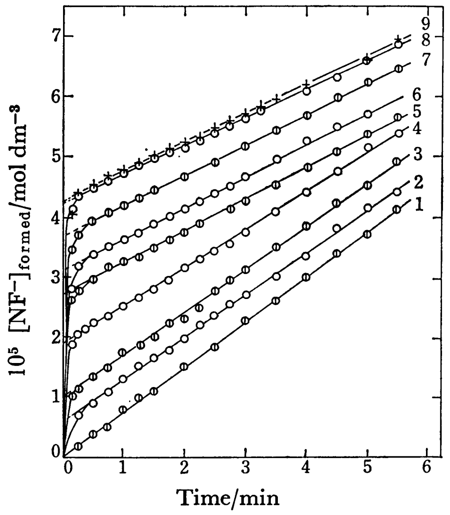

Fig. 6. An example for the kinetic behavior in the addition of tetranitromethane to the copper(II)–thiosulfate mixture after a certain time of standing. The standing time of the mixture is 0, 1, 2, 5, 10, 20, 30, 60, and 120 min for curves 1, 2, 3, 4, 5, 6, 7, 8, and 9, respectively. $1.0\times10^{-4}$ mol dm$^{-3}$ tetranitromethane; $1.0\times10^{-4}$ mol dm$^{-3}$ in copper(II) sulfate; 20 °C; the other conditions are the same as in Table 2.

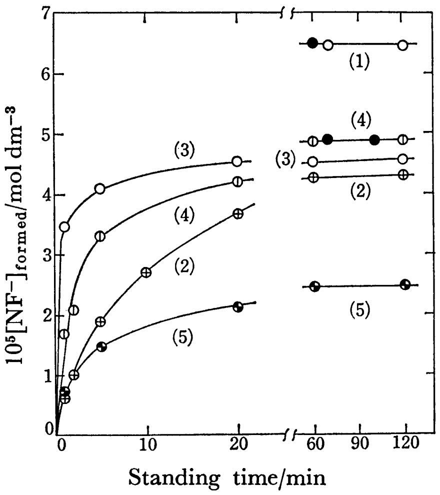

Fig. 7. The values extrapolated to time-zero in the plots of [NF$^-$]$_{\mathrm{formed}}$ *vs.* $t$ were plotted against time of standing. Conditions are $1.0\times10^{-4}$ mol dm$^{-3}$ tetranitromethane, ionic strength 0.2 mol dm$^{-3}$, 20 °C, and pH 4.7 with 0.2 mol dm$^{-3}$ sodium acetate-0.1 mol dm$^{-3}$ perchloric acid for curves 1 and 2, and with 0.02 mol dm$^{-3}$ sodium acetate-0.01 mol dm$^{-3}$ perchloric acid for curves 3, 4, and 5. Other conditions are $1.0\times10^{-3}$ mol dm$^{-3}$ thiosulfate and $2.0\times10^{-4}$ mol dm$^{-3}$ copper(II) for curve 1; $1.0\times10^{-3}$ mol dm$^{-3}$ thiosulfate and $1.0\times10^{-4}$ mol dm$^{-3}$ copper(II) for curves 2 and 3; $5.0\times10^{-4}$ mol dm$^{-3}$ thiosulfate and $1.0\times10^{-4}$ mol dm$^{-3}$ copper(II) for curve 4; $1.0\times10^{-3}$ mol dm$^{-3}$ thiosulfate and $5.0\times10^{-5}$ mol dm$^{-3}$ copper(II) for curve 5. Plots of ● indicate the data in the absence of oxygen, by bubbling nitrogen gas through the copper(II)-thiosulfate mixture during time of standing.

atmospheric pressure, the copper(I)–thiosulfate species resulting from the reduction of the copper(II) ion in aqueous solution by excess thiosulfate are stable with respect to reoxidation by molecular oxygen to copper(II). Ryabchikov and Sil'nichinko[12] reported that thiosulfate in excess over copper(II) (thiosulfate: copper(II)>3 : 1) results in the reaction:

$$2CuSO_4 + 6Na_2S_2O_3 \longrightarrow 2Na_3[Cu(S_2O_3)_2] + Na_2S_4O_6 + 2Na_2SO_4.$$

The $S_4O_6^{2-}$ ion forms no complexes with the copper(I) ion. Thiosulfate concentrations in the present investigation were 2.5 to 25 times in excess of the copper(II) concentration, and so the conditions are similar to those used by Fouda *et al.*[10,11] and Ryabchikov and Sil'nichinko.[12]

Byerley *et al.*[13] reported that complicated reactions occur in the reaction between the copper(II) ion and thiosulfate ion. It appears however that such complicated reactions do not occur under the present conditions which are designed for extremely low concentrations of copper(II) and thiosulfate ions.

## References

1) D. W. Johnson and G. A. Salmon, *J. Chem. Soc., Faraday Trans.*, *1*, **73**, 256 (1977).

2) R. M. Sellers and M. G. Simic, *J. Chem. Soc., Chem. Commun*, **1975**, 401; *J. Am. Chem. Soc.*, **98**, 6145 (1976).

3) S. A. Chaudhri and K.-D. Asmus, *J. Chem. Soc., Faraday Trans.*, *1*, **68**, 385 (1972).

4) J. Rabani, W. A. Mulac, and M. S. Matheson, *J. Phys. Chem.*, **69**, 53 (1965).

5) K.-D. Asmus, S. A. Chaudhri, N. B. Nazhat, and W. F. Schmidt, *Trans. Faraday Soc.*, **67**, 2607 (1971).

6) A. Fojtik, G. Czapski, and Henglein, *J. Phys. Chem.*, **74**, 3204 (1970).

7) K.-D. Asmus, A. Henglein, M. Ebert, and J. P. Keene, *Ber. Bunsenges. Phys. Chem.*, **68**, 657 (1964).

8) R. W. Miller and C. T. Kerr, *J. Biol. Chem.*, **241**, 5597 (1966).

9) "Stability Constants of Metal-Ion Complexes," ed by L. G. Sillén and E. Martell, Chem. Soc. Special Publication No. 25, 1971, p. 251.

10) J. J. Byerley, S. A. Fouda, and G. L. Rempel, *J. Chem. Soc., Dalton Trans.*, **1975**, 1329.

11) S. A. Fouda, *M. A. Sc. Thesis*, *University of Waterloo*, 1972; cited in Ref. 10.

12) D. I. Ryabchikov and V. G. Sil'nichenko, *Bull. Acad. Sci. USSR*, *Classe Sci. Chim.*, **1947,** 19 ; *Chem. Abstr.*, **42**, 4477 (1948).

13) J. J. Byerley, S. A. Fouda, and G. L. Rempel, *J. Chem. Soc., Dalton Trans.*, **1973,** 889.

14) G. Åkerlöf, *J. Am. Chem. Soc.*, **54**, 4125 (1932).