Oxidation of Thiourea by Iodate: a New Type of Oligo-oscillatory Reaction

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In the oxidation of thiourea by iodate in weakly acidic solution the concentration of iodide may exhibit several extrema. The number of extrema mainly depends on the initial ratio of the concentrations of thiourea and iodate, and is at most four. The first step of the reaction results in the formation of iodide which then reacts with iodate to give iodine. The latter oxidizes thiourea in several steps, the end products being sulphate ions, ammonium ions, and carbon dioxide. Taking into account the independently determined rate constants for the sub-systems, the change in the concentrations of iodide and iodine with time can be calculated. There is good agreement between the experimental and theoretical curves.

It was recently discovered[1] that the oxidation of hydroxylamine both by iodate and periodate exhibits oligo-oscillatory kinetics: the maximum number of extrema on a plot of iodide concentration *versus* time is three. We had thought that oligo-oscillatory reactions might be found when both the oxidizing and reducing centres may occur in different oxidation states and therefore the stoicheiometry of the reaction would depend on the ratio of the initial concentrations of the reactants. Thus we hoped to find such unusual kinetics in the oxidation of compounds containing sulphur in its lower oxidation states with halogenates. Exploratory experiments indicated that several extrema on the curves of iodide concentration *versus* time occur when for example diethyldithiocarbamate or thiourea is oxidized with iodate in a weakly acidic medium.

In this paper the results of a kinetic study of the iodate–thiourea and the iodine–thiourea systems are described. The stoicheiometry of the former reaction has been studied by Nurakhmetov *et al.*[2] According to them, when iodate is in excess, the stoicheiometry is as in equation (i), while if the ratio (R) of $[\text{thiourea}]_0/[\text{iodate}]_0$ exceeds 3:1 equation (ii) is valid.

$$5\,CS(NH_2)_2 + 8\,HIO_3 + 6\,H_2O \longrightarrow 5\,(NH_4)_2SO_4 + 5\,CO_2 + 4\,I_2 \quad \text{(i)}$$

$$3\,CS(NH_2)_2 + HIO_3 + 6\,H_2O \longrightarrow 3\,S + 3\,(NH_4)_2CO_3 + HI \quad \text{(ii)}$$

Although our experiments are in complete agreement with the findings of Nurakhmetov *et al.* in the case of an excess of iodate, we have clear-cut evidence that equation (ii) does not describe the stoicheiometry of this most complex reaction. Iodate is reduced to iodide, but the distribution of the oxidized products depends on the kinetic parameters of a number of reactions.

Experimental

All chemicals were of analytical grade and used without further purification. Redistilled water was employed for solutions, except for iodine where acetic acid was used as a solvent. The concentration of stock solutions were 0.1 mol dm^{-3}. All solutions were deoxygenated by bubbling argon through them. The reactions were initiated by injecting a small volume of thiourea solution into a mixture of the other reagents. The iodide-ion concentration was monitored using a Radelkis OP-I 7112D iodide-selective electrode, with a saturated calomel electrode (s.c.e.) as reference, and a Radiometer PHM 64 pH meter. The s.c.e. was connected to the reaction mixture *via* an agar–agar salt bridge prepared with saturated KNO_3. This was necessary to prevent chloride ions from entering the reaction mixture, which would disturb the reaction through reaction with iodate. The iodide-selective electrode was standardized with KI solutions containing thiourea, iodine, and acetic acid in the same concentrations as employed in the reaction.

The sum of the concentrations of I_2 and I_3^- was determined spectrophotometrically at the isosbestic point (468 nm, ε = 740 dm^3 mol^{-1} cm^{-1}) using a Beckman Acta III spectrophotometer. In order to maintain constant the ionic strength and pH, the concentration of acetic acid was 0.4 mol dm^{-3} in each case. All kinetic measurements were made at 25 ± 0.1 °C.

Results and Discussion

The Kinetics of Oxidation of Thiourea by Iodate.—The change in iodide concentration with time at different initial concentration ratios (R) of thiourea and iodate is shown in Figure 1. When the thiourea is present in high excess, the concentration of iodide monotonously increases to a limiting value; in the case of excess of iodate, the concentration of iodide exhibits just one maximum. However, if R is in the range 0.6–3:1 more than one maximum occur. Figure 2 shows the change in the number of extrema as a function of R.

At low values of R there is only one extremum, obviously a maximum. Upon increasing R, three extrema are found in the concentration *versus* time curve. There is no possibility of two extrema occurring in this range of R, since the iodide concentration at both the initial and the final stage of the reaction is

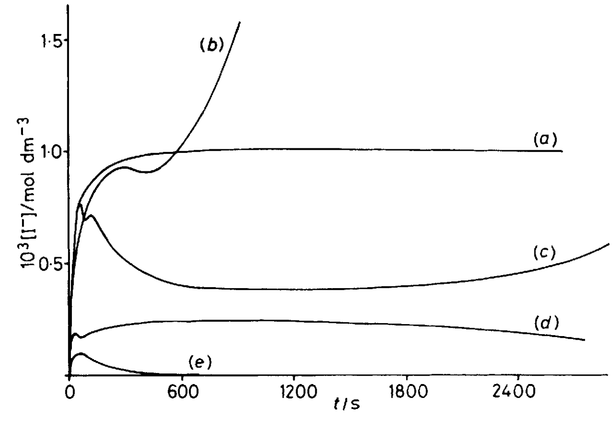


Figure 1. The concentration of iodide *vs.* time in the iodate–thiourea reaction. $[\text{thiourea}]_0$ = 0.005, $[IO_3^-]_0$ = 0.001 (*a*), 0.0025 (*b*), 0.005 (*c*), 0.007 (*d*), and 0.010 mol dm^{-3} (*e*)

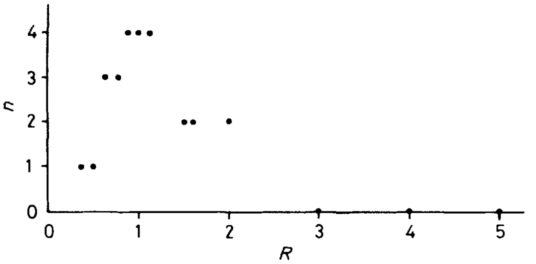


Figure 2. The number of extrema as a function of the ratio of [thiourea]$_0$ to [iodate]$_0$. [thiourea]$_0$ = 0.005 mol dm^{-3}

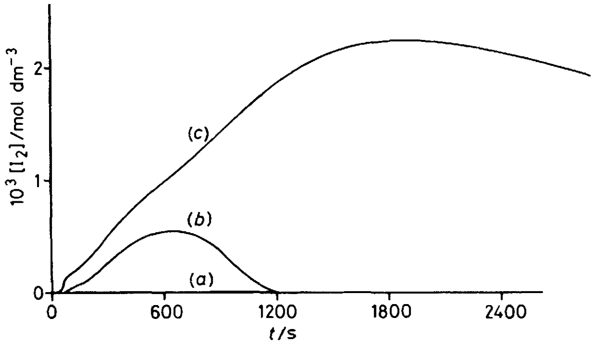
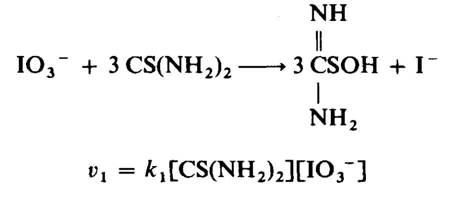


Figure 3. The concentration of iodine *vs.* time in the iodate–thiourea reaction. [thiourea]$_0$ = 0.005, [IO$_3^-$]$_0$ = 0.001 (*a*), 0.0025 (*b*), and 0.005 mol dm^{-3} (*c*)

practically zero, therefore the number of extrema must be uneven. Upon further increasing *R*, the final concentration of iodide is finite, therefore the last extremum can be either a maximum or a minimum, and the total number of extrema can be even or uneven. In this system only an even number of extrema has been found experimentally and calculations have given the same result.

The change in iodine concentration with time at different values of *R* is shown in Figure 3. At the smallest concentration of iodate (*R* = 5) no formation of iodine could be detected. At *R* = 2 there is almost a 1 min time lag and the maximum is preceded by an inflexion point. By further increasing the iodate concentration the time lag decreases, the shoulder is more definite, and the maximum concentration of iodine is much higher. When iodate is present in excess (*R* < 0.6) the concentration of iodine monotonously increases to a limiting value. At these ratios and absolute concentrations the formation of iodine cannot be followed spectrophotometrically since solid iodine is precipitated from the solution.

The fact that iodide is formed before iodine and sulphur makes it very likely that iodate is reduced by thiourea in three consecutive steps, the first being the rate-determining one [equation (1)]. In (1′) and subsequent rate equations the



$$\mathrm{IO_3^- + 3\,CS(NH_2)_2 \longrightarrow 3\,\underset{\underset{NH_2}{|}}{\overset{\overset{NH}{\|}}{C}}SOH + I^-} \qquad (1)$$

$$v_1 = k_1[\mathrm{CS(NH_2)_2}][\mathrm{IO_3^-}] \qquad (1')$$

hydrogen-ion concentration is not included since in all experiments it was kept constant. Therefore, the rate constants are valid only for this particular hydrogen-ion concentration. The rate constant k_1 can be estimated from the initial rate of the iodide production as 1 dm^3 mol^{-1} s^{-1}.

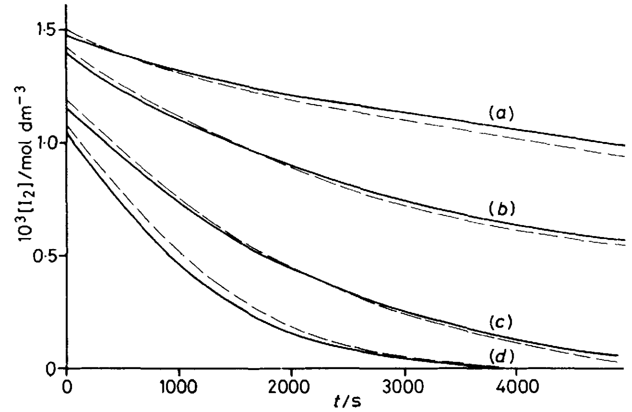


Figure 4. Kinetic curves for the iodine–thiourea reaction. [I$_2$]$_0$ = 0.0016, [thiourea]$_0$ = 0.00015 (*a*), 0.0003 (*b*), 0.00075 (*c*), and 0.0010 mol dm^{-3} (*d*). ———, Exptl., ———, calc.

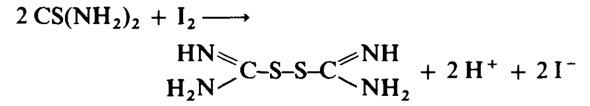
Iodine is then produced in the reaction between iodate and iodide [equation (2)]. The rate of this (the Dushman) reaction under the given experimental conditions is given in equation (2′)

$$\mathrm{IO_3^- + 5\,I^- + 6\,H^+ \longrightarrow 3\,I_2 + 3\,H_2O} \qquad (2)$$

$$v_2 = k_2[\mathrm{IO_3^-}][\mathrm{I^-}]^2 \qquad (2')$$

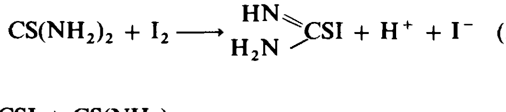
where k_2 = 4 150 dm^6 mol^{-2} s^{-1}. The appearance of iodine clearly indicates that for a quantitative description of the reaction the oxidation of thiourea by iodine also should be taken into consideration. Therefore the kinetics of the iodine–thiourea reaction have also been studied.

The Kinetics of the Oxidation of Thiourea by Iodine.— As is seen from Figure 4, the first step of the reaction, in which 1 mol iodine is consumed by 2 mol of thiourea, is very fast. According to stopped-flow experiments, the rate constant is larger than 2 × 10^4 dm^3 mol^{-1} s^{-1}. A mechanism consistent with rate equation (3′) is given by two consecutive reactions (3a) and (3b).

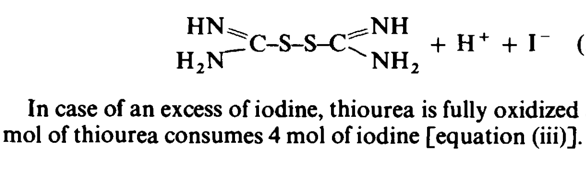


$$\mathrm{2\,CS(NH_2)_2 + I_2 \longrightarrow (HN{=})(H_2N)C{-}S{-}S{-}C({=}NH)(NH_2) + 2\,H^+ + 2\,I^-} \qquad (3)$$

$$v_3 = k_3[\mathrm{CS(NH_2)_2}][\mathrm{I_2}] \qquad (3')$$



$$\mathrm{CS(NH_2)_2 + I_2 \longrightarrow (HN{=})(H_2N)CSI + H^+ + I^-} \qquad (3a)$$



$$\mathrm{(HN{=})(H_2N)CSI + CS(NH_2)_2 \longrightarrow (HN{=})(H_2N)C{-}S{-}S{-}C({=}NH)(NH_2) + H^+ + I^-} \qquad (3b)$$

In case of an excess of iodine, thiourea is fully oxidized and 1 mol of thiourea consumes 4 mol of iodine [equation (iii)].

$$\mathrm{CS(NH_2)_2 + 4\,I_2 + 7\,H_2O \longrightarrow SO_4^{2-} + CO_3^{2-} + 8\,I^- + 2\,NH_4^+ + 10\,H^+} \qquad (iii)$$

As is seen from the curves in Figure 5, iodide is a strong inhibitor of the oxidation of thiourea by iodine. This inhibi-

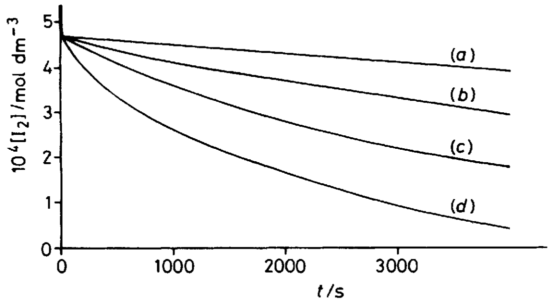
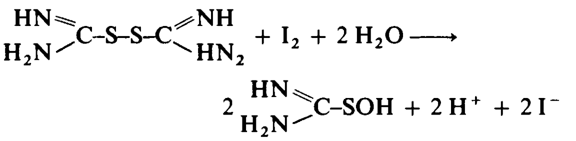
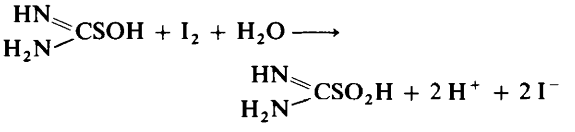


Figure 5. Effect of iodide ion on the rate of the iodine–thiourea reaction. $[\text{thiourea}]_0 = 1.5 \times 10^{-4}$, $[I_2] = 5.43 \times 10^{-4}$, $[I^-]_0 = 0.05$ (*a*), 0.025 (*b*), 0.005 (*c*), and 0.0005 mol dm^{-3} (*d*)

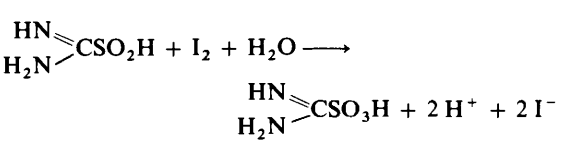
tory effect is obviously due to the formation of triiodide ion which oxidizes thiourea much more slowly than does iodine. The curves in Figure 4 can be quantitatively described by assuming a stepwise oxidation of dithiobisformamidine by iodine [equations (4)—(7)]. Triiodide ion is involved in a very fast equilibrium (8). In the calculations the analogous oxidation reactions of triiodide ion were disregarded.


$$(HN)(H_2N)C\text{-}S\text{-}S\text{-}C(NH)(HN_2) + I_2 + 2\,H_2O \longrightarrow 2\,(HN)(H_2N)C\text{-}SOH + 2\,H^+ + 2\,I^- \qquad (4)$$

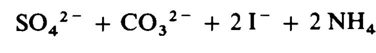
$$v_4 = k_4[(HN)(H_2N)CS_2C(NH_2)(NH)][I_2],\quad k_4 = 3.6\ \text{dm}^3\ \text{mol}^{-1}\ \text{s}^{-1} \qquad (4')$$


$$(HN)(H_2N)CSOH + I_2 + H_2O \longrightarrow (HN)(H_2N)CSO_2H + 2\,H^+ + 2\,I^- \qquad (5)$$

$$v_5 = k_5[(HN)(H_2N)CSOH][I_2],\quad k_5 = 50\ \text{dm}^3\ \text{mol}^{-1}\ \text{s}^{-1} \qquad (5')$$


$$(HN)(H_2N)CSO_2H + I_2 + H_2O \longrightarrow (HN)(H_2N)CSO_3H + 2\,H^+ + 2\,I^- \qquad (6)$$

$$v_6 = k_6[(HN)(H_2N)CSO_2H][I_2],\quad k_6 = 0.2\ \text{dm}^3\ \text{mol}^{-1}\ \text{s}^{-1} \qquad (6')$$


$$(HN)(H_2N)CSO_3H + I_2 + 4\,H_2O \longrightarrow SO_4^{2-} + CO_3^{2-} + 2\,I^- + 2\,NH_4^+ + 4\,H^+ \qquad (7)$$

$$v_7 = k_7[(HN)(H_2N)CSO_3H][I_2],\quad k_7 = 0.1\ \text{dm}^3\ \text{mol}^{-1}\ \text{s}^{-1} \qquad (7')$$

$$I_2 + I^- \rightleftharpoons I_3^- \qquad (8)$$

$$v_8 = k_8[I_2][I^-], k_8 = 4.1 \times 10^{10}\ \text{dm}^3\ \text{mol}^{-1}\ \text{s}^{-1}$$
$$v_{-8} = k_{-8}[I_3^-], k_{-8} = 7.6 \times 10^7\ \text{s}^{-1} \qquad (8')$$

Description of the Oligo-oscillatory Reaction.—As shown in Figures 6 and 7, the change in concentrations of iodide and iodine as a function of time can be described by taking into consideration rate equations (1′)—(8′). Obviously, the further oxidation of the dithiobisformamidine, sulphenic, sulphinic, and sulphonic acid derivatives by iodate also can take place, but the experiments suggest that these reactions are much slower than the corresponding oxidations by iodine and therefore their contribution can be neglected. In the calculations the differential equations (9)—(18) are solved.

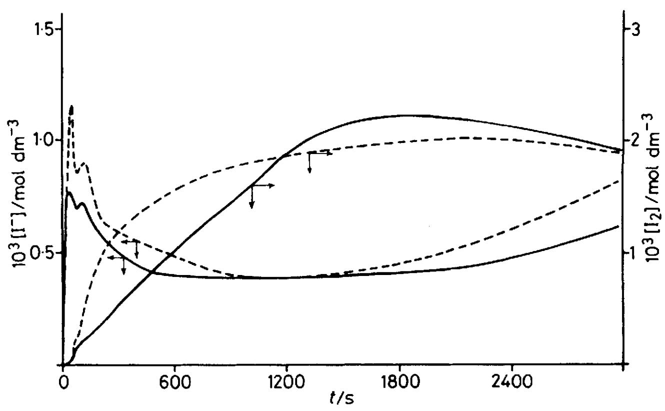


Figure 6. Kinetic curves for the iodate–thiourea reaction. The full lines indicate experimentally measured values, dashed lines the calculated ones. $[IO_3^-] = 0.005$, $[\text{thiourea}]_0 = 0.005$ mol dm^{-3}

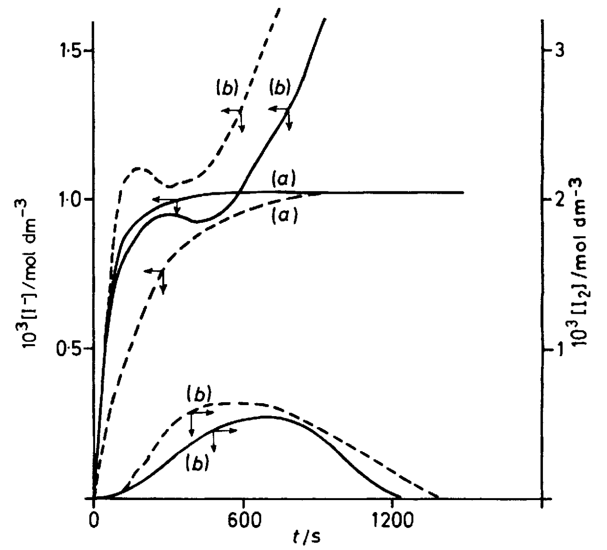


Figure 7. Experimental (——) and calculated kinetic curves (- - - -) for the iodate–thiourea reaction. $[\text{thiourea}]_0 = 0.005$, $[IO_3^-] = 0.001$ (*a*) and 0.0025 mol dm^{-3} (*b*)

$$d[I_2]/dt = 3v_2 - v_3 - v_4 - v_5 - v_6 - v_7 - v_8 + v_{-8} \qquad (9)$$

$$d[I^-]/dt = v_1 - 5v_2 + 2v_3 + 2v_4 + 2v_5 + 2v_6 + 2v_7 - v_8 + v_{-8} \qquad (10)$$

$$d[IO_3^-]/dt = -v_1 - v_2 \qquad (11)$$

$$d[I_3^-]/dt = v_8 - v_{-8} \qquad (12)$$

$$d[CS(NH_2)_2]/dt = -3v_1 - 2v_3 \qquad (13)$$

$$d[(HN)(H_2N)CS_2C(NH_2)(NH)]/dt = v_3 - v_4 \qquad (14)$$

$$d[(HN)(H_2N)CSOH]/dt = 3v_1 + 2v_4 - v_5 \qquad (15)$$

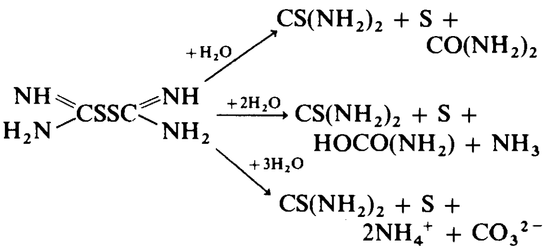
$$d[(HN)(H_2N)CSO_2H]/dt = v_5 - v_6 \quad (16)$$

$$d[(HN)(H_2N)CSO_3H]/dt = v_6 - v_7 \quad (17)$$

$$\frac{d[SO_4{}^{2-}]}{dt} = \frac{d[CO_3{}^{2-}]}{dt} = \frac{d[NH_4{}^+]}{dt} = v_7 \quad (18)$$

Although the agreement between the experimentally found and calculated values is not perfect, it is reassuring that the calculations describe exactly the change in number of extrema as a function of the concentrations of the reactants, and the characteristic initial part of the iodine concentration *versus* time curves. The rather large differences between the experimental and calculated iodine concentrations in the later stages of the reaction are probably due to the weak interactions of iodine with a number of species in the reaction mixture, which drastically influence the absorbance of the solution.

In case of excess of thiourea, the cloudiness of the solutions indicates the formation of trace amounts of elemental sulphur. However, it is obvious that sulphur does not form in the reaction (ii) suggested by Nurakhmetov *et al.*, since iodide is formed much in advance of sulphur. The formation of sulphur is a side reaction, and its extent is so small that it can be completely disregarded in the quantitative description of the iodide and iodine concentrations as a function of time. The most likely source of the sulphur is the hydrolytic disproportionation of dithiobisformamidine [equations (19)—(21)].



$$(HN)(H_2N)CSSC(NH)(NH_2) \xrightarrow{+H_2O} CS(NH_2)_2 + S + CO(NH_2)_2 \quad (19)$$

$$(HN)(H_2N)CSSC(NH)(NH_2) \xrightarrow{+2H_2O} CS(NH_2)_2 + S + HOCO(NH_2) + NH_3 \quad (20)$$

$$(HN)(H_2N)CSSC(NH)(NH_2) \xrightarrow{+3H_2O} CS(NH_2)_2 + S + 2NH_4{}^+ + CO_3{}^{2-} \quad (21)$$

The main source of the oligo-oscillatory behaviour of this system is the rather distinct stepwise oxidation of sulphur from the oxidation state −2 to +6 by iodine. One may expect similar behaviour in the iodate oxidation of different thiols which can be oxidized beyond the disulphide stage. According to Danehy[3] several β-mercaptocarboxylic acids are susceptible to such 'overoxidation,' and therefore the study of the iodate oxidation of these compounds may lead to the discovery of further oligo-oscillatory reactions.

Experiments concerning the hydrogen-ion dependence of the iodate–thiourea reaction are in progress.

Acknowledgements

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