

KINETIC STUDIES OF THIOCYANATE AND IODIDE OXIDATION WITH 2,6-DICHLOROQUINONE-4-CHLORO-IMIDE. A NOVEL AND A NEW OXIDIZING AGENT

V. NEERAJA, R. VENAKATA NADH, B. SYAMA SUNDAR*, P. S. RADHAKRISHNAMURTI

Department of Chemistry, Nagarjuna University, Nagarjunanagar 522510, India

ABSTRACT

The kinetics of oxidation of thiocyanate and iodide with a novel and mild oxidizing agent, namely 2,6-dichloroquinone-4-chloro-imide, has been studied. 2,6-dichloroquinone-4-chloro-imide undergoes hydrolysis and yields hypochlorous acid (HOCl) and 2,6-dichloro-*p*-benzoquinone. In both reactions with thiocyanate and iodide the main oxidation sequence is with hypochlorous acid. The second oxidation sequence with 2,6-dichloroquinone with these substrates is very much slower. All the observed facts have been rationalized taking into account the presence of the two active oxidizing species.

AIMS AND BACKGROUND

The kinetics of oxidation of thiocyanate ion by a variety of oxidants under catalyzed and uncatalyzed conditions has been well reported in literature¹⁻⁹. The authors have reported the oxidation products as CN⁻ and CNO⁻ along with SO₄²⁻ with different oxidants. In a few cases the product identified is the dimer (SCN)₂. Similarly the kinetics of oxidation of iodide with a variety of oxidizing agents like V(V) and Ce(IV) has been well documented¹⁰⁻¹².

It is of interest to study the use of 2,6-dichloroquinone-4-chloro-imide as an oxidizing agent with a few inorganic substrates like thiocyanate and iodide as the oxidation sequences will be consecutive, firstly by the hydrolyzed HOCl and later by 2,6-dichloro-*p*-benzoquinone, the other hydrolytic product.

EXPERIMENTAL

2,6-dichloroquinone-4-chloro-imide: Fluka (Purum) grade sample was used as a stock solution in glacial acetic acid.

Thiocyanate and iodide: BDH AnalaR samples were used without further purification.

All other chemicals, acids and solvents used in these investigations were of analytical reagent grade.

* For correspondence.

KINETIC METHOD

Reaction between thiocyanate and 2,6-dichloroquinone-4-chloro-imide. Aliquots in the reaction mixture were analyzed by iodometric method. 5.0 ml of the reaction mixture containing 2,6-dichloroquinone-4-chloro-imide was pipetted out at various intervals of time into a mixture of iodate free KI solution containing dilute sulphuric acid (2N) in a carbon dioxide atmosphere. The liberated iodine was titrated against standard thiosulphate solution to the disappearance of the blue starch-iodine end point.

Reaction between iodide and 2,6-dichloroquinone-4-chloro-imide. The liberated iodine is estimated by the standard thiosulphate solution to the disappearance of blue starch-iodine end point.

Some kinetic runs were followed by analysis with a spectrophotometer. The rate constants obtained by both methods were with an accuracy of $\pm 2\%$.

STOICHIOMETRY

With iodide. In stoichiometric experiments employing $[\text{oxidant}]_0 > [\text{substrate}]_0$ (example: $[\text{ox}]_0$ is $0.001 \text{ mol dm}^{-3}$; $[\text{S}]_0$ is $0.0005 \text{ mol dm}^{-3}$ potassium iodide; HOAc and water 20:80%; NaOAc is 0.2 mol dm^{-3} and temperature 30°C) the liberation of iodine is monitored until concentration of liberated iodine becomes constant. It was found that two moles of substrate required one mole of 2,6-dichloroquinone-4-chloro-imide (equivalent to one mole of HOCl formed due to hydrolysis of one mole of 2,6-dichloroquinone-4-chloro-imide), in accordance with the overall reaction as follows:



With thiocyanate. In stoichiometric experiments employing $[\text{oxidant}]_0 > [\text{substrate}]_0$ (example: $[\text{ox}]_0 = 0.002 \text{ mol dm}^{-3}$; $[\text{S}]_0 = 0.00025 \text{ mol dm}^{-3}$, HOAc and water 20:80%; $[\text{HClO}_4] = 0.05 \text{ mol dm}^{-3}$ and temperature 30°C) the disappearance of the oxidant was monitored until a constancy in the value of left over oxidant was found. It was found that two moles of substrate required one mole of 2,6-dichloroquinone-4-chloro-imide, in accordance with the overall reaction as follows:

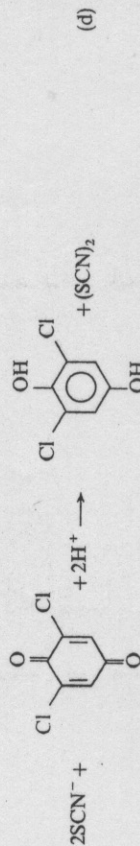
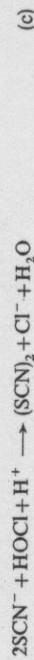
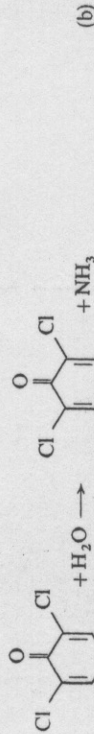
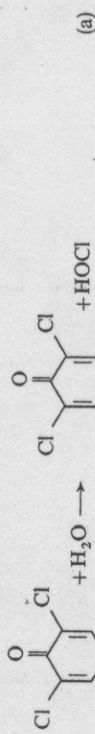


RESULTS AND DISCUSSION

Reaction between thiocyanate and 2,6-dichloroquinone-4-chloro-imide. It was of interest to study the kinetics of oxidation of thiocyanate by a new oxidizing agent, i.e. 2,6-dichloroquinone-4-chloro-imide. This reagent gives rise to two oxidizing species HOCl and 2,6-dichloroquinone with diverse redox potentials in subsequent stages of hydrolysis. Hence two reaction sequences occur: (1) with HOCl and (2) with 2,6-dichloroquinone. When large excess of the oxidant is used the main reaction is between the substrate and HOCl. On the contrary, when large excess of the substrate is used till the equality of the concentrations of the

substrate and the oxidant the two reaction sequences occur: the first is a reasonably fast step involving thiocyanate and HOCl, and the second one is a slow reaction involving thiocyanate and 2,6-dichloroquinone. Approximately the rate of the second oxidation reaction by quimone is about 50 times slower compared to the first oxidation reaction by HOCl. This is quite in accordance with the redox potentials of HOCl and 2,6-dichloroquinone, respectively. This is the first example being reported in literature regarding the oxidation of SCN^- by consecutive sequences of oxidation by an oxidizing agent involving N-halo derivatives.

The sequences of reaction are:



Reaction (c) is the main oxidation reaction involving SCN^- and the hydrolyzed species of 2,6-dichloroquinone-4-chloro-imide, namely HOCl, whereas reaction (d) is a consecutively very slow reaction involving SCN^- and 2,6-dichloroquinone. The relevant kinetic data is given in Table I. The reported kinetic rate constants belong to the oxidation sequence by the hydrolyzed HOCl as the consecutive sequence of oxidation by 2,6-dichloroquinone is very slow. The following facts emerge from the above data.

1. The reaction is mainly between the hydrolyzed species of 2,6-dichloroquinone-4-chloro-imide and SCN^- . The consecutive reaction of oxidation of SCN^- by 2,6-dichloroquinone is very slow, about 60 to 70 times slower than the former reaction.
2. The reaction is first order in the oxidant, in the substrate and in H^+ leading to an independence at higher concentrations of $[\text{H}^+]$. The reaction is catalyzed by Mn^{2+} . The increase of percentage of AcOH increases the kinetic rate. The addition of perchlorate ion enhances the rate. The addition of chloride ion also enhances the rate.

Table 1. Kinetic data in case of oxidation of thiocyanate with 2,6-dichloroquinone-4-chloro-imide (oxidant) at temperature 30°C

Variant	Concentration of non-variant	Concentration of variant (mol dm ⁻³)	k ₁ × 10 ⁴ (s ⁻¹)
Oxidant	[SCN ⁻] = 0.0005 mol dm ⁻³	0.00025	7.5
	[HClO ₄] = 0.05 mol dm ⁻³	0.0005	8.3
	AcOH = 5%	0.00075	8.3
		0.00025	20.55
Oxidant	[SCN ⁻] = 0.0005 mol dm ⁻³	0.0005	24.5
	[HClO ₄] = 0.05 mol dm ⁻³	0.00075	19.0
	AcOH = 10%	0.001	19.0
		0.002	19.5
SCN ⁻	[oxidant] = 0.002 mol dm ⁻³	0.00025	8.5
	[HClO ₄] = 0.05 mol dm ⁻³	0.0005	17.0
	AcOH = 20%	0.001	40.0
		0.001	2.7
HClO ₄	[oxidant] = 0.0005 mol dm ⁻³	0.0025	5.2
	[SCN ⁻] = 0.002 mol dm ⁻³	0.005	9.6
	AcOH = 10%	0.01	8.7
		0.01	8.7
Mn(II)	[oxidant] = 0.0005 mol dm ⁻³	zero	7.5
	[SCN ⁻] = 0.0005 mol dm ⁻³	0.0005	22.5
	[HClO ₄] = 0.05 mol dm ⁻³	0.001	34.0
	AcOH = 5%	0.001	34.0
NaClO ₄	[oxidant] = 0.0005 mol dm ⁻³	zero	7.5
	[SCN ⁻] = 0.0005 mol dm ⁻³	0.001	19.0
	[HClO ₄] = 0.05 mol dm ⁻³	0.001	19.0
	AcOH = 5%	0.001	19.0

3. The replacement of HClO₄ by sodium acetate results in retardation. The rates (k₁) in the presence of 0.05 mol dm⁻³ HClO₄ and in the presence of 0.02 mol dm⁻³ AcONa are found to be 0.001135 s⁻¹ and 0.0001043 s⁻¹, respectively under similar experimental conditions (i.e. [2,6-dichloroquinone-4-chloro-imide] = 0.005 mol dm⁻³, [SCN⁻] = 0.0005 mol dm⁻³, AcOH = 5%).

4. In few experiments where the excess substrate is used it is possible to compute the kinetic rates of the consecutive reactions namely (1) thiocyanate and HOCl (2) thiocyanate and 2,6-dichloroquinone occurring consecutively by the reactive species formed by the hydrolysis of 2,6-dichloroquinone-4-chloro-imide. The procedure for the computation of rate constants for the two consecutive reactions is as follows:

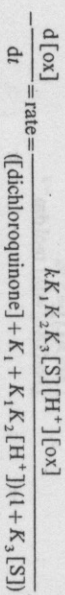
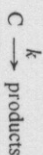
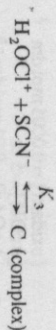
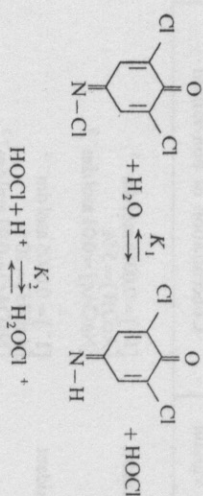
The rate constant of the first reaction was computed from the rate data up to 40% of the reaction in a kinetic run. The second step rate constant was computed from the rate data between 55 to 70% of the reaction. The rate data of the consecutive steps is given in Table 2.

Table 2. Rate data for the consecutive oxidations of thiocyanate with 2,6-dichloroquinone-4-chloro-imide

[SCN ⁻] (mol dm ⁻³)	Rate of I step oxidation k ₁ × 10 ⁴ (s ⁻¹)	Rate of II step oxidation k ₁ ' × 10 ⁴ (s ⁻¹)
0.0005	7.5	0.1124
0.001	9.7	0.135
0.002	17.0	0.398
0.004	35.0	0.7

[2,6-dichloroquinone-4-chloro-imide] = 0.0005 mol dm⁻³, [HClO₄] = 0.05 mol dm⁻³, AcOH = 5%, temperature 30°C.

The sequence of the reaction for the main oxidation process is as follows:



If the concentration of dichloroquinone term in the denominator is small and negligible when compared to other terms the kinetic rate is given by:

$$\frac{d[\text{ox}]}{dt} = \text{rate} = \frac{kK_1K_2K_3[\text{S}][\text{H}^+][\text{ox}]}{[\text{dichloroquinone}] + K_1 + K_1K_2[\text{H}^+](1 + K_3[\text{S}])}$$

Reaction between iodide and 2,6-dichloroquinone-4-chloro-imide. As a continuation we investigated the oxidation of iodide ion by this versatile oxidizing agent 2,6-dichloroquinone-4-chloro-imide at pH 2.82 to 4.12. The reaction is very smooth. At this pH the reaction is mainly the oxidation of iodide by N-halo derivative and the subsequent consecutive oxidation by 2,6-dichloroquinone does not take place at this pH. Hence by choosing a particular pH 3 to 4 one can study the exclusive oxidation of the substrate by 2,6-dichloroquinone-4-chloro-imide without interference from any oxidation by the liberated 2,6-dichloroquinone. The relevant rate data is given in Table 3.

The consideration of the data in Table 3 leads to the following:

1. The reaction is first order in the oxidant, in the substrate, near first order in H⁺.

2. The reaction is mainly between iodide and the hydrolyzed species of 2,6-dichloroquinone-4-chloro-imide, namely HOCl. There is absolutely no reaction between iodide and 2,6-dichloroquinone, the second hydrolytic species at these acetic acid-sodium acetate buffer conditions.

3. The increase of percentage of acetic acid increases the kinetic rate. The mechanistic sequences are as follows:

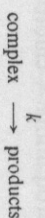
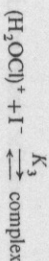
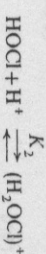
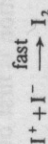
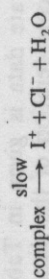


Table 3. Kinetic data in case of oxidation of iodide with 2,6-dichloroquinone-4-chloro-imide (oxidant) at temperature 30°C

Variant	Concentration of non-variant	Concentration of variant (mol dm ⁻³)	k ₁ × 10 ⁴ (s ⁻¹)
Oxidant	[I ⁻] = 0.0015 mol dm ⁻³	0.00025	6.722
	[AcOH] = 5%	0.0005	8.528
	[NaOAc] = 0.01 mol dm ⁻³	0.00075	7.573
Oxidant	[I ⁻] = 0.0005 mol dm ⁻³	0.00025	7.123
	[AcOH] = 20%	0.0005	7.722
	[NaOAc] = 0.02 mol dm ⁻³	0.0015	7.834
I ⁻	[oxidant] = 0.0005 mol dm ⁻³	0.0005	7.461
	[AcOH] = 5%	0.0005	2.378
	[NaOAc] = 0.01 mol dm ⁻³	0.0015	6.77
I ⁻	[oxidant] = 0.0005 mol dm ⁻³	0.0005	8.528
	[AcOH] = 5%	0.0005	13.72
	[NaOAc] = 0.01 mol dm ⁻³	0.004	27.838
AcOH	[oxidant] = 0.0005 mol dm ⁻³	0.0005	0.3598
	[AcOH] = 5%	0.001	0.6525
	[NaOAc] = 0.1 mol dm ⁻³	0.005	4.332
AcOH	[I ⁻] = 0.0005 mol dm ⁻³	0.01	11.6877
	[oxidant] = 0.0005 mol dm ⁻³	0.02	25.045
	[NaOAc] = 0.02 mol dm ⁻³	5%	1.918
AcOH	[I ⁻] = 0.001 mol dm ⁻³	10%	4.4909
	[oxidant] = 0.0005 mol dm ⁻³	20%	7.772
	[NaOAc] = 0.02 mol dm ⁻³	30%	9.077
NaOAc	[I ⁻] = 0.001 mol dm ⁻³	10.25%	8.0259
	[oxidant] = 0.0005 mol dm ⁻³	13.75%	12.724
	[NaOAc] = 0.02 mol dm ⁻³	23.75%	18.009
NaOAc	[I ⁻] = 0.001 mol dm ⁻³	38.75%	26.715
	[AcOH] = 5%	0.01	6.77
	[oxidant] = 0.0005 mol dm ⁻³	0.05	1.2281
		0.1	0.6525
		0.2	0.3838

This explains the observed kinetic orders. The complex decomposition may be visualised as follows:



$$\text{rate} = \frac{kK_1K_2K_3[S][\text{H}^+][\text{ox}]}{([\text{dichloroquinone}] + K_1 + K_1K_2[\text{H}^+])(1 + K_3[S])}$$

If the concentration of dichloroquinone term in the denominator is small and negligible when compared to other terms the kinetic rate is given by:

$$\text{rate} = \frac{kK_2K_3[S][\text{ox}][\text{H}^+]}{(1 + K_2[\text{H}^+])(1 + K_3[S])}$$

CONCLUSION

The consideration of the observed kinetic data of both the thiocyanate and iodide with 2,6-dichloroquinone-4-chloro-imide shows that this new N-halo derivative is

a mild oxidizing agent which is capable of affecting oxidations smoothly of many inorganic systems, like hydroxylamine and hydrazine. Preliminary experiments with both systems indicate that the rate measurements are very smooth compared to the earlier studies of these nitrogen derivatives and metallic oxidizing agents like Cr(VI), Ce(IV), V(V) and even with oxy anions, like bromate, periodate and iodate.

REFERENCES

1. I. R. WILSON, G. H. HARRIS: *J. Am. Chem. Soc.*, **82**, 4515 (1960).
2. I. R. WILSON, G. H. HARRIS: *J. Am. Chem. Soc.*, **83**, 286 (1961).
3. FORDSMITH, HABIB: *J. Chem. Soc. (Dalton)*, 461 (1973).
4. U. MURALIKRISHNA, K. V. BAPANAJAH: *Indian J. Chem.*, **25B**, 225 (1975).
5. D. S. MAHADEVAPPA, B. T. GOWDA, N. M. GOWDA: *Z. Nature. Forsch.*, **32B**, 52 (1979).
6. D. M. STANBURY, W. K. WIOLMARK, S. KHALAF, H. N. PO, J. E. BYOD: *Inorg. Chem.*, **19**, 2715 (1980).
7. P. S. RADHAKRISHNAMURTI, S. P. MISRA, J. K. PANDA: *Indian J. Chem.*, **20A**, 459 (1981).
8. A. RAMESH, B. SYAMA SUNDAR, P. S. RADHAKRISHNAMURTI: *Asian J. Chem.*, **8**(4), 599 (1996).
9. A. RAMESH, B. SYAMA SUNDAR, P. S. RADHAKRISHNAMURTI: *Oxid. Commun.*, **20**(2), 1997.
10. C. G. SWAIN, K. HEDBERG: *J. Am. Chem. Soc.*, **72**, 3373 (1950).
11. E. L. KING, M. L. PANDOW: *J. Am. Chem. Soc.*, **75**, 3063 (1953).
12. R. VENKATA NADH, B. SYAMA SUNDAR, P. S. RADHAKRISHNAMURTI: *Asian J. Chem.*, **9**(3), 55 (1997).

Received 15 August 1997
Revised 26 December 1997