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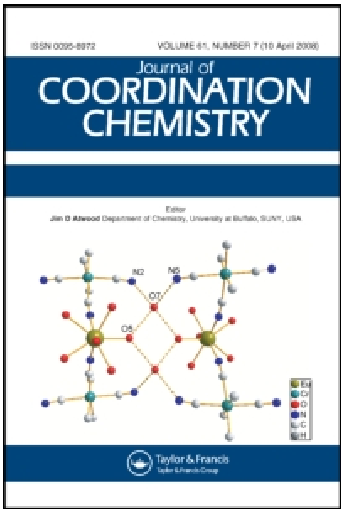

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Hassan A. Ewais[a]; Mohamed A. Nagdy[a]; Ahmed A. Abdel-Khalek[a]
[a] Faculty of Science, Chemistry Department, Beni-Suef University, Beni-Suef City, Egypt

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Kinetics and mechanism of oxidation of the binary and ternary complexes of chromium(III) involving inosine and glycine by *N*-bromosuccinimide

HASSAN A. EWAIS, MOHAMED A. NAGDY† and
AHMED A. ABDEL-KHALEK*

Faculty of Science, Chemistry Department, Beni-Suef University, Beni-Suef City, Egypt

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The kinetics of oxidation of the chromium(III) complexes, $[Cr(Ino)(H_2O)_5]^{3+}$ and $[Cr(Ino)(Gly)(H_2O)_3]^{2+}$ (Ino = Inosine and Gly = Glycine) involving a ligands of biological significance by *N*-bromosuccinimide (NBS) in aqueous solution to chromium(VI) have been studied spectrophotometrically over the 25–45°C range. The reaction is first order with respect to both [NBS] and [Cr], and increases with pH over the 6.64–7.73 range in both cases. The experimental rate law is consistent with a mechanism in which the hydroxy complexes $[Cr(Ino)(H_2O)_4(OH)]^{2+}$ and $[Cr(Ino)(Gly)(H_2O)_2(OH)]^{+}$ are significantly more reactive than their conjugate acids. The value of the intramolecular electron transfer rate constant, k_1, for the oxidation of the $[Cr(Ino)(H_2O)_5]^{3+}$ ($6.90 \times 10^{-4}\,s^{-1}$) is lower than the value of k_2 ($9.66 \times 10^{-2}\,s^{-1}$) for the oxidation of $[Cr(Ino)(Gly)(H_2O)_2]^{2+}$ at 35°C and $I = 0.2\,mol\,dm^{-3}$. The activation parameters have been calculated. Electron transfer apparently takes place via an inner-sphere mechanism.

Keywords: Inosine; Glycine; Chromium(III); Oxidation; *N*-bromosuccinimide

1. Introduction

Interest on chromium(III) complexes with nucleotides arises from the use of these complexes as enzymatic labels by substitution of the activator or inhibitor [1, 2] and finding the role of chromium(III) in transcription processes and RNA and DNA interactions [3]. The oxidation of chromium from +3 to +6 is an important environmental process because of the high mobility and toxicity of chromium(VI) [4]. Chromium(VI) compounds are well known to be potent toxic and carcinogenic agents [4]. Because chromium(VI) is easily taken up by cells and is subsequently reduced to the trivalent form, the formation of chromium(III) or other intermediate oxidation states such as chromium(V) and (IV) is believed to play a role in the adverse biological effects of chromium(VI) compounds [4].

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*Corresponding author. Email: hslalby2002@yahoo.com
†Abstracted from the MSc thesis of Mohamed A. Nagdy.

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N-bromosuccinimide (NBS) has been used widely as a brominating and oxidizing agent for organic compounds. It was reported that the oxidation process proceeds via bromonium ion Br^+ [5] in a polar medium or, alternatively, by a free radical path involving the homolytic dissociation of NBS [6, 7].

Oxidation of metal complexes by NBS has received little attention [8–15]. Inner-sphere oxidations of $[CrEDTA]^{2-}$ [8], $[Cr(H_2O)_6]^{3+}$ [9], $[Cr(EDDA)(H_2O)_2]^+$ (EDDA = ethylenediaminediacetate) [10], $[Cr(NTA)(H_2O)_2]$ [11] (NTA = nitrilotriacetate), $[Cr(H_2O)(TOH)]$ [12] (TOH = *N*-(2-hydroxyethyl)ethylenediamine-*N*,*N*,*N*-triacetate) and $[Cr(L)_2(H_2O)_2]^{3+}$ [13] (L = 2-aminomethylpyridine) by NBS were studied. The reactions were found to proceed *via* a mechanism in which coordinated water was replaced by NBS prior to electron transfer.

The kinetics of oxidation of $[Cr(Dpc)_2(H_2O)_2]^-$ [14] (Dpc = dipicolinic acid) and $[Cr(Dpc)(Asp)(H_2O)_2]$ [15] (Asp = aspartic acid) by NBS were investigated. It was found that the secondary ligand, aspartic acid, makes the ternary complex $[Cr(Dpc)(Asp)(H_2O)_2]$ more oxidizable by NBS than the binary complex $[Cr(Dpc)_2(H_2O)_2]^-$.

In this article, the kinetics of oxidation of $[Cr(Ino)(H_2O)_5]^{3+}$ and $[Cr(Ino)(Gly)(H_2O)_3]^{2+}$ (Ino = Inosine and Gly = Glycine) are reported in order to study the effect of complex formation of the binary and ternary complexes on the rate parameters for oxidation of these Cr(III) complexes and to find optimal conditions for oxidation of these important complexes.

2. Experimental

2.1. *Materials and solutions*

Binary and ternary complexes, $[Cr(Ino)(H_2O)_5]^{3+}$ and $[Cr(Ino)(Gly)(H_2O)_3]^{2+}$ were prepared by the reported method [16]. All chemicals used in this study were of reagent grade (Analar, BDH, Sigma). Freshly prepared solutions of NBS were used. Buffer solutions were made from Na_2HPO_4 and NaH_2PO_4. $NaNO_3$ was used to adjust the ionic strength of the buffered solutions. Doubly distilled H_2O was used in all kinetic runs.

Decomposition of $[Cr(Ino)(H_2O)_5]^{3+}$ and $[Cr(Ino)(Gly)(H_2O)_3]^{2+}$ at the pH of study was checked, no change of spectra, peaks or molar absorptivity of these complexes occurred during the time of reaction.

2.2. *Oxidation products*

The ultraviolet visible absorption spectra of the oxidation products of $[Cr(Ino)(H_2O)_5]^{3+}$ and $[Cr(Ino)(Gly)(H_2O)_3]^{2+}$ by NBS were recorded over time on a JASCO UV-530 spectrophotometer (figures 1 and 2). The data show that the chromium(III)-complex peaks at 575 and 567 nm for $[Cr(Ino)(H_2O)_5]^{3+}$ and $[Cr(Ino)(Gly)(H_2O)_3]^{2+}$ have disappeared and been replaced by a peak at 360 nm. The spectrum and molar absorptivity of the final product were the same as that of chromate ion, proving that chromium(VI) is the oxidation product.

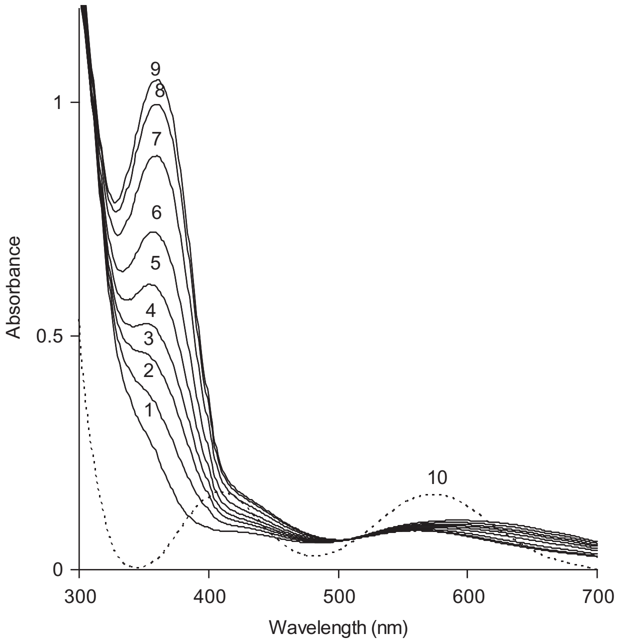

Figure 1. Change in absorbance as a function of time. Curves (1)–(9) were recorded at 1, 3, 5, 8, 12, 15, 22, 30 and 40 min respectively, from the time of initiation; [complex] = 1.0×10^{-3} M, [NBS] = 0.02 M, $I = 0.2$ M, pH = 7.38 and $T = 35$°C. Curve (10) (------), spectrum of the complex (1.0×10^{-3} M) at the same pH.

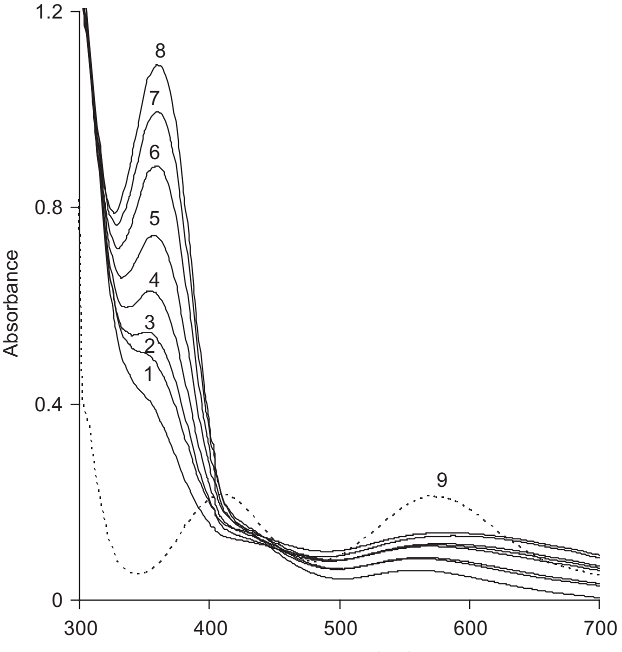

Figure 2. Change in absorbance as a function of time. Curves (1)–(8) were recorded at 2, 5, 7, 12, 15, 20, 25 and 32 min, respectively, from the time of initiation; [complex] = 1.0×10^{-3} M, [NBS] = 0.02 M, $I = 0.2$ M, pH = 7.38 and $T = 35$°C. Curve (9) (-------), spectrum of the complex (1.0×10^{-3} M) at the same pH.

2.3. *Stoichiometry*

A known excess of chromium(III)-complex was added to an NBS solution. The absorbance of chromium(VI) produced was measured at 360 nm 24 h after the onset of the reaction. The number of moles of the chromium(III) complex consumed was calculated using the molar absorptivity of chromate [17].

2.4. *Kinetic procedures*

The ultraviolet visible absorption spectra of the reaction solutions during oxidation of $[Cr(Ino)(H_2O)_5]^{3+}$ and $[Cr(Ino)(Gly)(H_2O)_3]^{2+}$ by NBS were followed spectrophotometrically for a definite period of time using the JASCO UV-530 spectrophotometer. The reaction mixture was prepared as follows: 10 mL (0.2 M NaH_2PO_4 + 0.2 M Na_2HPO_4) + 1.6 mL 2.0 M $NaNO_3$ + 1.0 mL 0.01 M complex + 4.0 mL 0.2 M NBS (added at the beginning of reaction) were made up to a total volume to 40 mL by deionized water, thermally equilibrated for ca 15 min. in an automatic circulation thermostat, thoroughly mixed and quickly transferred to an absorption cell. The oxidation rates were measured by monitoring the absorbance of Cr(VI) at 360 nm, on a Milton–Roy 601 spectrophotometer, where the absorption of the oxidation products is maximal at the reaction pH. The pH of the reaction mixture was measured using a Chertsey Surrey, 7065 pH-meter.

The temperature of the reacting solution was controlled, using an automatic circulation thermostat. The thermostat was provided with a special pumping system for circulating water at regulated temperature in the cell holder. The average stabilizing accuracy as measured in the thermostat liquid was ±0.1°C.

Pseudo-first order conditions were maintained in all runs by the presence of a large excess (>10-fold) of NBS. The ionic strength was kept constant by the addition of $NaNO_3$ solution. The pH of the reaction mixture was found to be always the same pH at the beginning and end of the runs.

Potentiometric measurements were performed with a Metrohm 702 SM titrino, using Irving and Rossotti techniques [18].

3. Results and discussion

3.1. *1-Kinetics of $[Cr(Ino)(H_2O)_5]^{3+}$/NBS reaction*

Oxidation of $[Cr(Ino)(H_2O)_5]^{3+}$ was studied over the 6.64–7.73 pH range, 0.1 mol dm^{-3} ionic strength, $(0.3\text{–}3.0) \times 10^{-2}$ mol dm^{-3} NBS and 25–45°C (±0.1°C). The overall stoichiometry of the reaction was 1.9 ± 0.1 moles of NBS per mole of chromium(III) within the time of reaction. Hence the reaction is described by equation (1).

$$Cr^{III} + 2NBS \longrightarrow Cr(VI) + 2Br^- + \text{other product} \qquad (1)$$

Plots of $\ln(A_\infty - A_t)$ *versus* time were linear up to 80% of reaction where A_t and A_∞ are absorbance at time t and time infinity, respectively. Pseudo-first order rate constants, k_{obs}, obtained from the slopes of these plots, are collected in table 1. The results (table 1) show that k_{obs} was unaffected when the concentration of the

Table 1. Dependence of k_{obs} on [NBS] at different temperatures at pH = 7.38, $[Cr(Ino)(H_2O)_5^{3+}]^a = 2.5 \times 10^{-4}\,mol\,dm^{-3}$, and $I = 0.2\,mol\,dm^{-3}$ (Error = 2–4%).

10^2 [NBS] ($mol\,dm^{-3}$)	$10^4\,k_{obs}$ (s^{-1})				
	25°C	30°C	35°C	40°C	45°C
0.3	0.075	0.15	0.39	0.81	1.54
0.5	0.11	0.26	0.67	1.42	2.95
1.0	0.16	0.37	1.07	2.23	4.25
1.5	0.23	0.50	1.40	3.42	6.28
2.0	0.30	0.68	2.01	4.20	8.30
2.5	0.34	1.03	2.67	5.60	10.40
3.0	0.36	1.12	3.07	6.32	12.50

[a] $[Cr^{III}(Ino)(H_2O)_5^{3+}] = 2.5 \times 10^{-4}\,mol\,dm^{-3}$; $10^4\,k_{obs} = 2.05$, 1.95, 2.12 and 2.09 s^{-1} at $10^4\,[Cr^{III}(Ino)(H_2O)_5^{3+}]$ of 1.25, 3.75, 5.0 and 6.25 $mol\,dm^{-3}$ respectively at 35°C and $[NBS] = 0.02\,mol\,dm^{-3}$.

chromium(III)-complex was varied at constant NBS concentration, indicating first order dependence on complex concentration.

At constant $[H^+]$ and ionic strength, $1/k_{obs}$ varies linearly with 1/[NBS] at different temperatures (figure 3), and the kinetics of the reaction are described by equation (2):

$$d[Cr(VI)]/dt = \{a[NBS]_T/1 + b[NBS]_T\} + [Cr^{III}]_T \tag{2}$$

and

$$k_{obs} = a[NBS]_T/(1 + b[NBS]_T) \tag{3}$$

or

$$1/k_{obs} = 1/a[NBS]_T + b/a \tag{4}$$

Plots of $1/k_{obs}$ *versus* 1/[NBS] at different pHs (6.64–7.73) (figure 4), show that the rate of reaction increases with increasing pH (table 2). The values of $10^4\,k_{obs}$, 2.02, 2.23, 2.07 and 2.11 s^{-1} at $I = 0.2$, 0.3, 0.4 and 0.5 $mol\,dm^{-3}$, pH = 7.38, $[NBS] = 0.02\,mol\,dm^{-3}$ and $T = 35°C$ indicate that k_{obs} is unaffected by ionic strength, implying that the reaction takes place between charged and uncharged species.

In aqueous solution the complex may be involved in the equilibrium shown in equation (5):

$$[Cr(Ino)(H_2O)_5]^{3+} \rightleftharpoons [Cr(Ino)(H_2O)_4(OH)]^{2+} + H^+ K_1 \tag{5}$$

K_1 was obtained potentiometrically with the value of $(5.40 \pm 0.2) \times 10^{-7}$ at 35°C. It is clear from the value of K_1 and the pH dependence of the reaction rate (figure 4), that in pH range used the hydroxo complex is the reactive species in the rate-determining step.

The following mechanism is proposed:

$$[Cr(Ino)(H_2O)_5]^{3+} \rightleftharpoons [Cr(Ino)(H_2O)_4(OH)]^{2+} + H^+ K_1 \tag{6}$$

$$[Cr(Ino)(H_2O)_4(OH)]^{2+} + NBS \rightleftharpoons [Cr(Ino)(H_2O)_3(OH)(NBS)]^{2+} + H_2O\ (fast)\ K_2 \tag{7}$$

$$[Cr(Ino)(H_2O)_4(OH)(NBS)]^{2+} \xrightarrow{k_1} Cr^{IV} + R^{\bullet} + Br^- + Ino \tag{8}$$

$$Cr^{IV} + R^{\bullet} \xrightarrow{fast} Cr^{V} + R^- \tag{9}$$

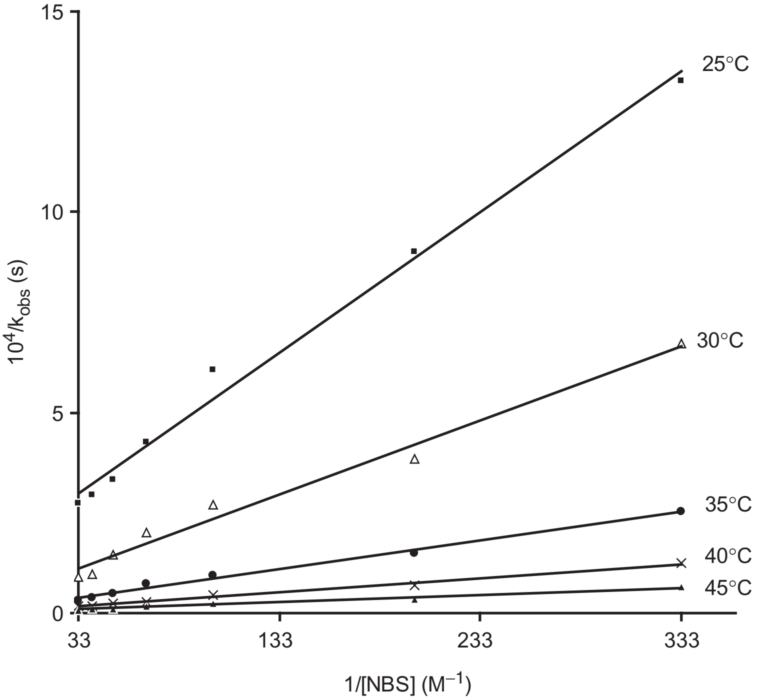

Figure 3. Plot $1/k_{\mathrm{obs}}$ *vs.* 1/[NBS] at different temperatures.

Table 2. Effect of pH on k_{obs} at $[\mathrm{Cr^{III}(Ino)(H_2O)_5}]^{3+} = 2.5 \times 10^{-4}\,\mathrm{mol\,dm^{-3}}$, $I = 0.2\,\mathrm{mol\,dm^{-3}}$ and $T = 35°\mathrm{C}$ (Error = 2–5%).

	$10^4\,k_{\mathrm{obs}}$ ($\mathrm{s^{-1}}$)			
10^2 [NBS] ($\mathrm{mol\,dm^{-3}}$)	pH = 6.64	pH = 6.96	pH = 7.38	pH = 7.73
0.3	0.10	0.20	0.39	0.93
0.5	0.17	0.35	0.67	1.32
1.0	0.32	0.65	1.07	2.02
1.5	0.42	0.90	1.40	2.70
2.0	0.53	1.08	2.01	3.33
2.5	0.83	1.46	2.67	4.25
3.0	1.02	1.82	3.07	4.98

$$\mathrm{Cr^V + NBS \xrightarrow{fast} Cr^{(IV)} + Br^- + R^\bullet} \tag{10}$$

$$\mathrm{R^\bullet + R^\bullet \longrightarrow R - R} \tag{11}$$

where $\mathrm{R^\bullet}$ is the succinimidyl radical.

That AgBr is formed and increases gradually with time during the reaction, supports the contention that $\mathrm{Br^-}$ is formed concurrently with the oxidation of chromium(III) to chromium(VI). Also, the fact that acrylonitrile is polymerized seems to support the formation of the succinimidyl radical. The succinimidyl radical may subsequently dimerize to give bissuccinimidyl [19, 20].

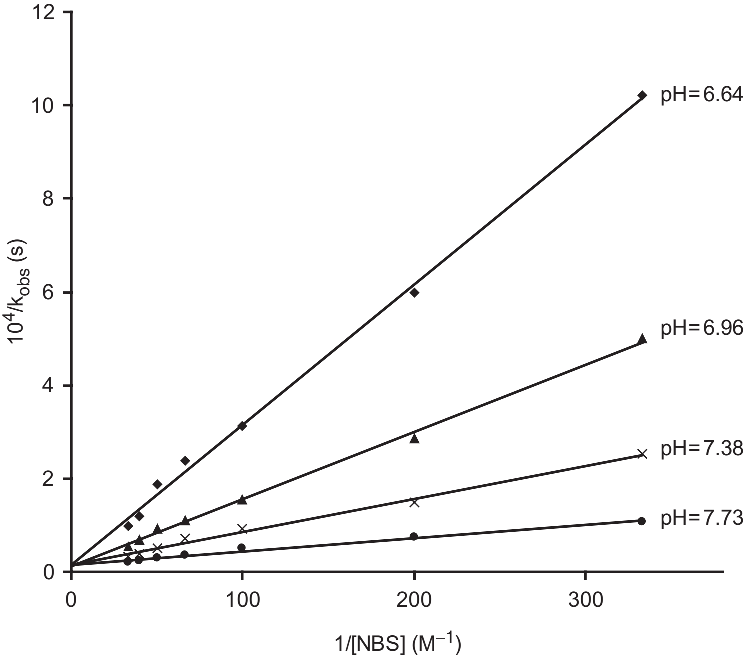

Figure 4. Plot of $1/k_{obs}$ *vs.* 1/[NBS] at different pH's.

From the above mechanism, the rate of the reaction is given by:

$$\text{Rate} = k_1K_2[\text{Cr(Ino)(H}_2\text{O)}_4\text{(OH)}]^{2+}[\text{NBS}] \tag{12}$$

If $[\text{Cr(III)}]_T$ represents the total concentration of chromium(III) species, then by rearrangement, one gets:

$$\begin{aligned}[\text{Cr(III)}]_T = {} & [\text{Cr(Ino)(H}_2\text{O)}_4\text{(OH)}^{2+}][\text{H}^+]/K_1 + [\text{Cr(Ino)(H}_2\text{O)}_4\text{(OH)}^{2+}] \\ & + K_2[\text{Cr(Ino)(H}_2\text{O)}_4\text{(OH)}^{2+}][\text{NBS}]\end{aligned} \tag{13}$$

substitution for $[\text{Cr(Ino)(H}_2\text{O)}_4\text{(OH)}^{2+}]$ from equation (13) into equation (12) gives:

$$\text{Rate} = k_1K_2[\text{NBS}][\text{Cr}]_T/\{([\text{H}^+]/K_1) + 1 + K_2[\text{NBS}]\} \tag{14}$$

$$k_{obs} = k_1K_2[\text{NBS}]/\{([\text{H}^+]/K_1) + 1 + K_2[\text{NBS}]\} \tag{15}$$

which on rearrangement, gives:

$$1/k_{obs} = ([H^+]/K_1) + 1 + K_2[\text{NBS}]/k_1K_2[\text{NBS}] \tag{16}$$

$$1/k_{obs} = ([H^+] + K_1) + K_1K_2[\text{NBS}]/k_1K_1K_2[\text{NBS}] \tag{17}$$

$$1/k_{obs} = K_1 + [H^+]/k_1K_1K_2[\text{NBS}] + 1/k_1 \tag{18}$$

At constant $[\text{H}^+]$, equation (18) is consistent with the experimental rate law shown in equation (4), where $a = k_1K_1K_2/K_1 + [\text{H}^+]$ and $b = K_1K_2/K_1 + [\text{H}^+]$.

Values of $10^4 k_1$ calculated from equation (18), are 0.55, 2.07, 6.90, 18.81 and 35.71 s^{-1} respectively at 25, 30, 35, 40, and 45°C. The activation parameters associated with k_1 obtained from a least-squares fit to the transition state theory equation are $\Delta H^* = (157.2 \pm 1.0)\,\mathrm{kJ\,mol^{-1}}$ and $\Delta S^* = (-203.3 \pm 3.0)\,\mathrm{J\,K^{-1}\,mol^{-1}}$.

From equation (18), it follows that the slope of the plots can be represented by equation (19)

$$\text{Slope} = [H^+]/k_1K_1K_3 + 1/k_1K_2 \tag{19}$$

It is obvious from equation (19) that the slope is dependent on $[\mathrm{H^+}]$. This plot is linear with a correlation coefficient of 0.9986. The values of K_1 and K_2 were calculated from equation (18) as $1.0 \times 10^{-7}\,\mathrm{mol\,dm^{-3}}$ and $142\,\mathrm{mol^{-1}\,dm^3}$ at 35°C and $I = 0.2\,\mathrm{mol\,dm^{-3}}$, respectively.

The value of K_1 is in good agreement with the obtained potentiometrically ($K_1 = 5.40 \times 10^{-7}$) at 35°C indicating the validity of our proposed mechanism.

3.2. *2-Kinetics of $[\mathrm{Cr(Ino)(Gly)(H_2O)_3}]^{2+}$/NBS reaction*

The stoichiometry of the reaction between $[\mathrm{Cr(Ino)(Gly)(H_2O)_5}]^{2+}$ and NBS in aqueous solution is represented by equation (20).

$$\mathrm{Cr(III)} + 2\mathrm{NBS} \longrightarrow \mathrm{Cr^{(VI)}} + 3\mathrm{Br^-} + \text{other product} \tag{20}$$

where Cr(III) and NBS are total Cr(III)-complex and NBS concentrations, respectively. The concentration of NBS initially present to [Cr(VI)] produced was found to be 2.00 : 1.00 The rate of oxidation of $[\mathrm{Cr(Ino)(Gly)(H_2O)_5}]^{2+}$ was studied at pH 6.64–7.73 pH and temperature 25–45°C over a range of NBS and complex concentrations.

First order plots of $\ln(A_\infty - A_t)$ *versus* time were linear for greater than 85% of the reaction. Observed rate constants, k_{obs}, obtained from the slopes of these plots, are collected in table 3. The magnitude of the observed pseudo first rate constant, k_{obs}, was independent of the chromium(III)-complex concentration as shown in table 3, indicating first order dependence on complex concentration.

At constant $[\mathrm{H^+}]$ and ionic strength, $1/k_{\mathrm{obs}}$ varies linearly with 1/[NBS] at different temperatures (figure 5), and the kinetics of the reaction are described by equation (2).

At constant temperature $1/k_{\mathrm{obs}}$ varies linearly with 1/[NBS] at different pHs (6.64–7.73) (figure 6), showing that the rate increases with increasing pH (table 4). The rate

Table 3. Dependence of k_{obs} on [NBS] at different temperatures at pH = 7.38, $[\mathrm{Cr(Ino)(Gly)(H_2O)_3^{2+}}]^{\mathrm{a}} = 2.5 \times 10^{-4}\,\mathrm{mol\,dm^{-3}}$, and $I = 0.2\,\mathrm{mol\,dm^{-3}}$ (Error = 2–5%).

	$10^4\,k_{\mathrm{obs}}\,(\mathrm{s^{-1}})$				
10^2 [NBS] ($\mathrm{mol\,dm^{-3}}$)	25°C	30°C	35°C	40°C	45°C
0.3	0.38	0.56	0.85	1.35	2.38
0.5	0.58	0.89	1.39	2.04	3.20
1.0	0.85	1.23	2.00	2.95	5.58
1.5	0.97	1.42	2.25	3.92	7.65
2.0	1.12	1.63	2.71	4.76	9.42
2.5	1.35	1.77	3.05	5.84	11.00
3.0	1.46	1.98	3.60	6.47	12.02

[a] $[\mathrm{Cr(Ino)(Gly)(H_2O)_3^{2+}}] = 2.5 \times 10^{-4}\,\mathrm{mol\,dm^{-3}}$; $10^4\,k_{\mathrm{obs}} = 2.65$, 2.59, 2.82 and $2.74\,\mathrm{s^{-1}}$ at $10^4\,[\mathrm{Cr(Ino)(Gly)(H_2O)_3^{2+}}]$ of 1.25, 3.75, 5.0 and $6.25\,\mathrm{mol\,dm^{-3}}$ respectively at 35°C and $[\mathrm{NBS}] = 0.02\,\mathrm{mol\,dm^{-3}}$.

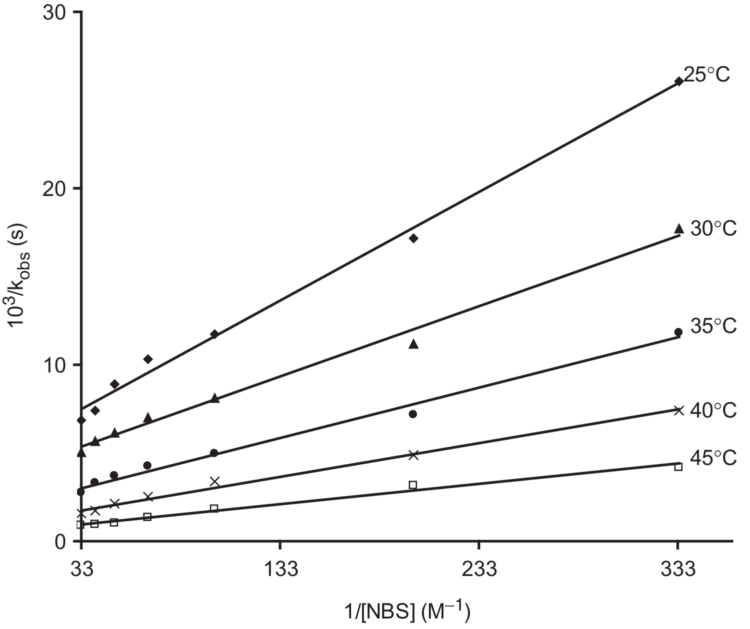

Figure 5. Plot of $1/k_{\mathrm{obs}}$ *vs.* 1/[NBS] at different temperatures.

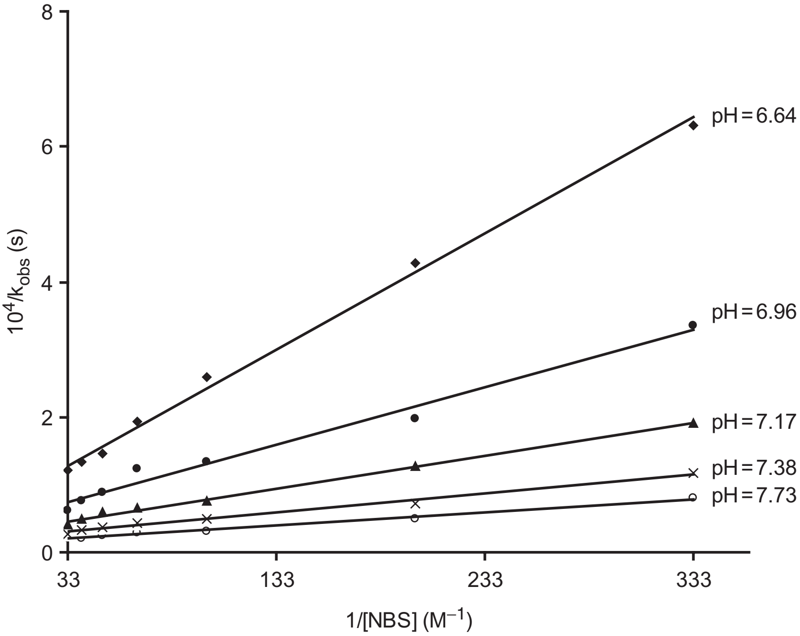

Figure 6. Plot of $1/k_{\mathrm{obs}}$ *vs.* 1/[NBS] at different pH's.

Table 4. Effect of pH on k_{obs} at $[Cr(Ino)(Gly)(H_2O)_3]^{2+} = 2.5 \times 10^{-4}$ mol dm^{-3}, $I = 0.2$ mol dm^{-3} and $T = 35°C$ (Error = 1–4%).

	$10^4 k_{obs}$ (s^{-1})				
10^2 [NBS] (mol dm^{-3})	pH = 6.64	pH = 6.93	pH = 7.17	pH = 7.38	pH = 7.73
0.3	0.16	0.30	0.52	0.85	1.25
0.5	0.23	0.05	0.78	1.39	2.04
1.0	0.38	0.75	1.32	2.00	3.24
1.5	0.52	0.81	1.52	2.25	3.56
2.0	0.68	1.13	1.70	2.71	3.98
2.5	0.75	1.32	2.05	3.05	4.73
3.0	0.83	1.62	3.38	3.60	5.00

constant k_{obs} is independent of the ionic strength (values of $10^4 k_{obs}$ of 2.71, 2.63, 2.82 and 2.70 s^{-1} were obtained at $I = 0.2$, 0.3, 0.4 and 0.5 mol dm^{-3}, pH = 7.38, [NBS] = 0.02 mol dm^{-3} and $T = 35°C$).

In aqueous solution the complex may be involved in the equilibrium shown in equation (21):

$$[Cr(Ino)(Gly)(H_2O)_3]^{2+} \rightleftharpoons [Cr(Ino)(Gly)(OH)(H_2O)_2]^{+} + H^{+}K_3 \tag{21}$$

K_3 was obtained potentiometrically with the value $(5.70 \pm 0.1) \times 10^{-7}$ at 35°C. From the pH range and K_3 value, the protonated species and its conjugated base prevail. From figure 6, the slope and intercept of the plot depend on pH, indicating the reaction proceeds through two paths, both dependent on $[H^+]$. The first path may involve the deprotonated form of the chromium(III)-complex $[Cr(Ino)(Gly)(OH)(H_2O)_2]^{+}$ and the second the protonated form $[Cr(Ino)(Gly)(H_2O)_3]^{2+}$. There are two possibilities for coordination of NBS. First, since the ligands weaken Cr–H_2O bonds, the H_2O ligand $[Cr(Ino)(Gly)(H_2O)_3]^{2+}$ may be substituted by NBS. Second, if the hydroxo form of the complex is the reactive species, the hydroxo ligand may bridge the two reactants [21]. The rate of reaction is independent of ionic strength, expected since the reaction takes place between charged and uncharged species.

The following mechanism is proposed:

$$[Cr(Ino)(Gly)(H_2O)_3]^{2+} \rightleftharpoons [Cr(Ino)(Gly)(OH)(H_2O)_2]^{+} + H^{+}(K_3) \tag{22}$$

$$[Cr(Ino)(Gly)(H_2O)_3]^{2+} + NBS \rightleftharpoons [Cr(Ino)(Gly)(H_2O)_2(NBS)]^{2+} + H_2O(K_4) \tag{23}$$

$$[Cr(Ino)(Gly)(OH)(H_2O)_2]^{+} + NBS \rightleftharpoons [Cr(Ino)(Gly)(OH)(NBS)(H_2O)_2)]^{2+} + (K_5) \tag{24}$$

$$[Cr(Ino)(Gly)(H_2O)_2(NBS)]^{2+} \longrightarrow Cr^{IV} + R^{\bullet} + Ino + Gly + Br^{-} + 2H_2O(k_2) \tag{25}$$

$$[Cr(Ino)(Gly)(OH)(NBS)(H_2O)_2]^{+} \longrightarrow Cr^{IV} + R^{\bullet} + Ino + Gly + Br^{-} + 2H_2O(k_3) \tag{26}$$

$$Cr^{IV} + R^{\bullet} \xrightarrow{\text{fast}} Cr^{V} + R^{-} \tag{27}$$

$$Cr^{V} + NBS \xrightarrow{\text{fast}} Cr^{(IV)} + Rr^{-} + R^{\bullet} \tag{28}$$

$$R^{\bullet} + R^{\bullet} \longrightarrow R - R \tag{29}$$

From the above mechanism the reaction rate is given by:

$$\mathrm{d}[\mathrm{Cr(VI)}]/\mathrm{d}t = (k_2K_4 + k_3K_5K_3/[\mathrm{H}^+])[\mathrm{Cr(Ino)(Gly)(H_2O)_3}]^{2+}[\mathrm{NBS}] \tag{30}$$

If $[\mathrm{Cr(III)}]_\mathrm{T}$ represents the total concentration of chromium(III) species, then:

$$\begin{aligned}[\mathrm{Cr(III)}]_\mathrm{T} = {} & [\mathrm{Cr(Ino)(Gly)(H_2O)_3}]^{2+} + (K_3/[\mathrm{H}^+])[\mathrm{Cr(Ino)(Gly)(H_2O)_3}]^{2+} \\ & + K_4[\mathrm{Cr(Ino)(Gly)(H_2O)_3}]^{2+}[\mathrm{NBS}] \\ & + (K_3K_5/[\mathrm{H}^+])[\mathrm{Cr(Ino)(Gly)(H_2O)_3}]^{2+}[\mathrm{NBS}]\end{aligned} \tag{31}$$

substitution for $[\mathrm{Cr(Ino)(Gly)(H_2O)_3}]^{2+}$ from equation (31) into equation (30) gives:

$$\begin{aligned}\mathrm{d}[\mathrm{Cr(VI)}]/\mathrm{d}t = {} & \{(k_2K_4 + k_3K_3K_5/[\mathrm{H}^+])[\mathrm{NBS}][\mathrm{Cr^{III}}]_\mathrm{T}\}/ \\ & \{1 + (K_3/[\mathrm{H}^+]) + (K_4 + K_3K_5/[\mathrm{H}^+])[\mathrm{NBS}]\}\end{aligned} \tag{32}$$

Hence:

$$\begin{aligned}k_\mathrm{obs} = {} & (k_2K_4 + k_3K_3K_5/[\mathrm{H}^+])[\mathrm{NBS}]/\{1 + (K_3/[\mathrm{H}^+]) \\ & + (K_4 + K_3K_5/[\mathrm{H}^+])[\mathrm{NBS}]\}\end{aligned} \tag{33}$$

$$k_\mathrm{obs} = (k_2K_4[\mathrm{H}^+] + k_3K_3K_5)[\mathrm{NBS}]/\{[\mathrm{H}^+] + K_3 + (K_4[\mathrm{H}^+] + K_3K_5)[\mathrm{NBS}]\} \tag{34}$$

H_2O is a weak bridge while OH^- is a very effective bridge in an inner-sphere process [21]. Therefore, $[\mathrm{Cr(Ino)(Gly)(OH)(NBS)(H_2O)_2}]^+$ is more reactive than $[\mathrm{Cr(Ino)(Gly)(H_2O)_2(NBS)}]^{2+}$. Thus, we can assume that $k_3K_3K_5 \gg k_2K_4$ $[\mathrm{H}^+]$ and equation (34) reduces to:

$$k_\mathrm{obs} = k_3K_3K_5[\mathrm{NBS}]/\{[\mathrm{H}^+] + K_3 + (K_4[\mathrm{H}^+] + K_3K_5)[\mathrm{NBS}]\} \tag{35}$$

On rearranging:

$$1/k_\mathrm{obs} = 1/[\mathrm{NBS}]\{[\mathrm{H}^+]/k_3K_3K_5 + 1/k_3K_5\} + \{K_4[\mathrm{H}^+]/k_3K_3K_5 + 1/k_3\} \tag{36}$$

At constant $[\mathrm{H}^+]$, equation (36) is consistent with the experimental rate law shown in equation (3), where

$$a = k_3K_3K_5/K_3 + [\mathrm{H}^+] \text{ and } b = (K_4\ [\mathrm{H}^+] + K_4K_5)/K_3 + [\mathrm{H}^+],$$

Plots of both $1/a = K_3 + [\mathrm{H}^+]/k_3K_5K_3$ and $b/a = (K_4\ [\mathrm{H}^+] + K_3K_5)/K_3K_5K_3$ *versus* $[\mathrm{H}^+]$ (figures 7 and 8) are linear with intercepts, consistent with the proposed mechanism.

The K_3 value, $2.2 \times 10^{-7}\,\mathrm{mol\,dm^{-3}}$ at 35°C, was calculated by dividing the intercept by the slope of figure 7. The intramolecular electron transfer rate constant, k_3, was calculated from the intercept of figure 8 as $9.66 \times 10^{-2}\,\mathrm{s^{-1}}$. The value of K_4 calculated by dividing the slope of figure 8 by that of figure 7 was $36.5\,\mathrm{mol^{-1}\,dm^3}$. Substituting the value of k_3 gives K_5 from the intercept of figure 7 as $81.8\,\mathrm{mol^{-1}\,dm^3}$. The K_3 value is in a good agreement with that obtained potentiometerically ($K_3 = 5.70 \times 10^{-7}$) at 35°C. Comparing the values of K_5 (81.8) and K_4 (36.5) provide justification for the suggested mechanism.

Activation parameters ΔH^* and ΔS^*, associated with constant (a) in equation 2, were obtained from a least-squares fit to the transition state theory equation as $59.3 \pm 0.4\,\mathrm{kJ\,mol^{-1}}$ and $-79.6 \pm 1.4\,\mathrm{J\,K^{-1}\,mol^{-1}}$ respectively. ΔH^* is a composite value including the enthalpy of formation associated with the precursor complex

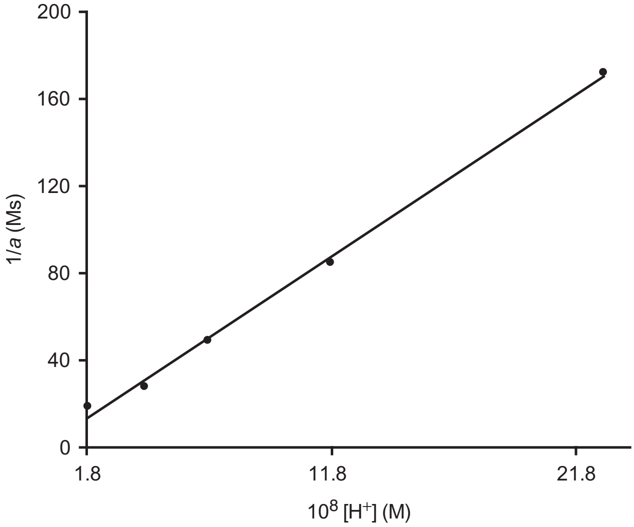

Figure 7. Plot of $1/a$ *vs*. $[H^+]$ at 35°C.

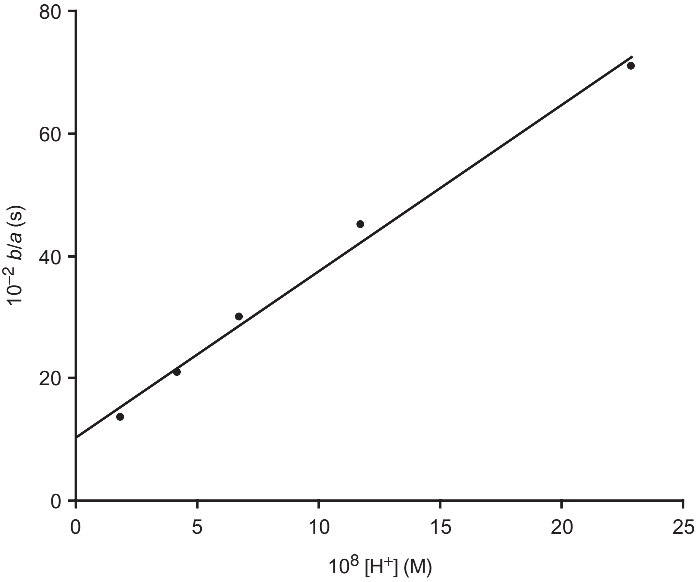

Figure 8. Plot of b/a *vs*. $[H^+]$ at 35°C.

$[Cr(Ino)(Gly)(H_2O)_3]^{2+}$ and enthalpy of activation of the intramolecular electron-transfer step.

Kinetics indicate oxidation of $[Cr(Ino)(H_2O)_5]^{3+}$ and $[Cr(Ino)(Gly)(H_2O)_3]^{2+}$ by *N*-bromosuccinamide proceeds through an inner sphere mechanism. This was supported by:

(a) The coordination of NBS to the metal is through the carbonyl group [9].
(b) No reaction was observed at $pH < 6$ where the hydroxo-species is not present.

In comparsion between the oxidation of $[Cr(Ino)(H_2O)_5]^{3+}$ and $[Cr(Ino)(Gly)(H_2O)_3]^{2+}$ under the same conditions, both hydroxy complexes $[Cr(Ino)(H_2O)_4(OH)]^{2+}$ and $[Cr(Ino)(Gly)(H_2O)_2(OH)]^{+}$ are significantly more reactive than their conjugate acids. The value of the intramolecular electron transfer rate constant, k_1, for oxidation of $[Cr(Ino)(H_2O)_5]^{3+}$ ($6.90 \times 10^{-4}\,s^{-1}$) is lower than the value of k_2 ($9.66 \times 10^{-2}\,s^{-1}$) for oxidation of $[Cr(Ino)(Gly)(H_2O)_2(OH)]^{2+}$ at 35°C and $I = 0.2\,mol\,dm^{-3}$. This may be due to the fact that glycine, as a secondary ligand, make the ternary complex $[Cr(Ino)(Gly)(H_2O)_2]^{2+}$ more oxidizable than $[Cr(Ino)(H_2O)_5]^{3+}$.

The high negative entropies of activation for these reactions were the result of the charge concentration on encounter complex formation, which causes substantial mutual ordering of the solvated water molecules [22]. The intramolecular electron transfer steps are endothermic as indicated by the value of ΔH^*. The contributions of ΔH^* and ΔS^* to the rate constant seem to compensate each other. This fact suggests that the factors controlling ΔH^* must be closely related to those controlling ΔS^*. Therefore, the solvation state of the encounter complex would be important in determining ΔH^* [22]. Thus, the relatively small enthalpy of activation, ΔH^*, can be explained in terms of the formation of a more solvated complex. The relatively low value of ΔH^* for $[Cr(Ino)(Gly)(H_2O)_2]^{2+}$ is due to its composite value including formation which may be exothermic and intramolecular electron transfer which may be endothermic.

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