J. Chem. Research (S),
1998, 558–559†

Effect of Ionic Strength on the Kinetics of the Oxidation of Ascorbic Acid by Hexacyanoferrate(III): Comparison between Specific Interaction Theories and the Mean Spherical Approximation†

T. Vilariño, P. Alonso, X. L. Armesto, P. Rodríguez and M. E. Sastre de Vicente*

*Dpto de Química Fundamental e Industrial, Facultad de Ciencias, Universidade da Coruña,
15071-A Coruña, Spain*

The influence of ionic strength on the rate constant of the oxidation reaction of ascorbic acid by hexacyanoferrate(III) in acidic medium is investigated. The dependence of the rate constant on ionic strength is discussed according to different specific interaction theories and the mean spherical approximation.

The reactivity of ascorbic acid is of great importance, mainly due to the biochemical significance of this species; numerous studies of the mechanisms of its oxidation by metal complexes have been undertaken.[1–3] On the other hand, this reaction has often been used in physical chemistry from an educational point of view.[4–7] In the present work the influence of ionic strength, in the range 0.05–2.0 M on the rate constant of oxidation of ascorbic acid by hexacyanoferrate(III) in acidic medium is investigated.

Some specific interaction models (SIT)[8,9] and also the mean spherical approximation (MSA), an integral equation based method,[10–13] have been employed in order to explain the variation of the logarithm of the rate constant (log *k*) with ionic strength.

Results and Discussion

The reaction was followed using a spectrophotometric method and pseudo-first-order conditions, *i.e.* at least a 10-fold excess of ascorbic acid. The corresponding first order plots were linear for at least three half lives of the reaction.

For the reduction of hexacyanoferrate(III) by ascorbic acid in acidic medium, a mechanism has been proposed which involves the attack of hexacyanoferrate(III) on the neutral ascorbic acid or the ascorbate anion (H_2A, HA^-) in a slow and rate determining step; this is followed by a fast step in which ascorbate radical-ion or ascorbate free radical, ($H_2A^{\bullet +}$, $HA^{\bullet}$) respectively, is attacked by a fresh hexacyanoferrate(III) ion to give the end product, dehydroascorbic acid:

$$H_2A + H_2O \overset{K_1}{\rightleftharpoons} HA^- + H_3O^+ \qquad (1)$$

$$HA^- + H_2O \overset{K_2}{\rightleftharpoons} A^{2-} + H_3O^+ \qquad (2)$$

$$H_2A + Fe(CN)_6{}^{3-} \xrightarrow{k_a} Fe(CN)_6{}^{4-} + H_2A^{\bullet +} \qquad (3)$$

$$HA^- + Fe(CN)_6{}^{3-} \xrightarrow{k_b} Fe(CN)_6{}^{4-} + HA^{\bullet} \qquad (4)$$

$$H_2A^{\bullet +} + Fe(CN)_6{}^{3-} \xrightarrow{\text{fast}} Fe(CN)_6{}^{4-} + A + 2H_3O^+ \qquad (5)$$

$$HA^{\bullet} + Fe(CN)_6{}^{3-} \xrightarrow{\text{fast}} Fe(CN)_6{}^{4-} + A + H_3O^+ \qquad (6)$$

In order to study the effect of ionic strength on the reaction rate, kinetic runs were performed with increasing concentrations of sodium perchlorate at different pH values. It was noted that the rate of the reaction strongly depends on pH since the latter controls the actual ascorbic acid/ascorbate species that participate in the rate-determining step. On the other hand, as the rate-determining step, for one of the reaction pathways, involves the collision between two anionic species, the rate constant is also influenced by the ionic strength of the medium which causes an alteration of the anionic atmosphere and changes the charge density around the anions.

From the above mechanism the rate of disappearance of hexacyanoferrate(III) is given by

$$\frac{d[Fe(CN)_6{}^{3-}]}{dt} = \frac{2k_a[H^+] + 2k_b K_1}{[H^+] + K_1}[H_2A]_T[Fe(CN)_6{}^{3-}] \qquad (7)$$

then

$$k_{obs} = \frac{2k_a[H^+] + 2k_b K_1}{[H^+] + K_1}[H_2A]_T \qquad (8)$$

In order to make a quantitative study of the ionic strength on the reaction rate, data obtained at $pH \approx 2$ were used, which, since $K_1 \ll [H^+]$, simplifies the denominator of eqn. (8). On the other hand, the pronounced dependence of rate constant on ionic strength, as well as the approximate reactivity ratio k_a/k_b of 10^{-4} suggested in the literature,[14] allow us to consider the first term in the numerator negligible and the expression for the observed rate constant becomes

$$k_{obs} = \frac{2k_b K_1 [H_2A]_T}{[H^+]} \qquad (9)$$

According to the proposed mechanism, the expression for log k_{obs} will be given by

$$\begin{aligned} \log k_{obs} &= \log 2k_b + \log K_1^* - \log[H^+] + \log \gamma_{AH^-} \\ &\quad + \log \gamma_{Fe(CN)_6{}^{3-}} - \log \gamma_{AC^‡} \\ &= \log 2k_b + \log K_1^T - 2\log \gamma_{\pm} - \log 10^{pH} + \log \gamma_{H^+} \\ &\quad + \log \gamma_{AH^-} + \log \gamma_{Fe(CN)_6{}^{3-}} - \log \gamma_{AC^‡} \end{aligned}$$

The effect of ionic strength on the rate constant has been studied by modelling the activity coefficients by use of some specific interaction models,[8,9] all based on the Debye–Hückel equation, and also a statistical mechanics treatment, the mean spherical approximation.[4,5,15] General equations for the calculation of activity coefficients by use of MSA appear in Table 1.

Substituting the activity coefficient expressions obtained from the different models the equations for the dependence of log k_{obs} on ionic strength (*I*) are shown in Table 2. As can be seen, MSA, contrary to SIT (Debye–Hückel, Pitzer, . . .), does not lead to analytical functions on ionic strength, but it is possible to take into account the size of the ions

---

*To receive any correspondence.

†This is a **Short Paper** as defined in the Instructions for Authors, Section 5.0 [see *J. Chem. Research (S)*, 1998, Issue 1]; there is therefore no corresponding material in *J. Chem. Research (M)*.

Table 1 General equations and parameters for calculation of activity coefficients by use of mean spherical approximation

General equations[4,5,15]	
Electrostatic contribution: Debye–Hückel type	$\ln \gamma_i^{\mathrm{el}} = -\frac{\alpha^2 \Gamma}{4\pi \sum_i \rho_i} \sum_i \frac{\rho_i z_i^2}{(1+\Gamma\sigma_i)} - \left[\frac{\alpha^2 z_i \sigma_i}{4(1+\Gamma\sigma_i)} - \frac{\pi\alpha^2\sigma_i^4\Gamma}{24(1+\Gamma\sigma_i)}\frac{P_n}{\Delta}\right]\frac{P_n}{\Delta}$
Hard-sphere contribution: Percus–Yevick equation	$\ln \gamma_i^{\mathrm{hs}} = -\ln\Delta + \frac{\sigma_i^3 X_0 + 3\sigma_i^2 X_1 + 3\sigma_i X_2}{\Delta} + \frac{3\sigma_i^3 X_1 X_2 + 9/2\,\sigma_i^2 X_2^2}{\Delta^2} + \frac{+3\sigma_i^3 X_2^3}{\Delta^3}$

Common parameters for all systems		Specific parameters for the studied system		
$\alpha^2 = \frac{4\pi e^2}{\varepsilon k T}$	$2\Gamma = \left[\alpha^2 \sum_{i=1}^{n} \frac{\rho_i z_i^2}{(1+\Gamma\sigma_i)^2}\right]^{1/2}$	Electric charges (z_i)	defined by the model	
$X_k = \frac{\pi}{6}\sum_i \rho_i \sigma_i^k$ ($k = 0,1,2,3$)	$P_n = \frac{1}{\Omega}\sum_i \frac{\rho_i \sigma_i z_i}{(1+\Gamma\sigma_i)}$	Numerical densities (ρ_i)	experimental conditions: constant ionic medium $\sum_i \rho_i = \rho_{\mathrm{Na^+}} + \rho_{\mathrm{ClO_4^-}} = 6.0225 \times 10^{-4}\ (2\ C_{\mathrm{NaClO_4}})$	
$\Delta = 1 - \frac{\pi}{6}\sum_i \rho_i \sigma_i^3$	$\Omega = 1 + \frac{\pi}{2\Delta}\sum_i \frac{\rho_i \sigma_i^3}{(1+\Gamma\sigma_i)}$	Ionic diameters (σ_i)	electrolyte ions[16]	$\sigma\ (\mathrm{ClO_4^-})$=4.79 Å (Pauling diameter) $\sigma\ (\mathrm{Na^+}) = 2.18 - 0.728 C_{\mathrm{NaCl_4}} + 0.0919 C^2_{\mathrm{NaClO_4}}$
constants	e: electron charge k: Boltzman constant T: temperature (K) ε: dielectric constant		reactive ions[17]	$\sigma\ ([\mathrm{Fe(CN_6)}]^{3-})$=8.8 Å $\sigma\ (\mathrm{C_6H_7O_6})$=7.0 Å $\sigma\ (\mathrm{AC^{\ddagger}})$=11.1 Å (optimized)

and the optimization of the diameters used. Details of the application of the method to studies of acid–base equilibria can be found in refs. 10–13.

Table 2 Dependence of log *k* on ionic strength according to several specific interactions models and the mean spherical approximation[a]

Equation type	log k_{obs}
Debye–Hückel	$C_1 + 7\frac{A\sqrt{I}}{1 + 2.5\sqrt{I}}$
Debye–Hückel + linear term	$C_2 + 7\frac{A\sqrt{I}}{1 + 2.17\sqrt{I}} + BI$
f^{γ} (Pitzer) + linear term	$C_3 + A'\left(\frac{\sqrt{I}}{1 + 1.2\sqrt{I}} + \frac{2}{1.2}\ln(1 + 1.2\sqrt{I})\right) + B'I$
Mean spherical approximation	$C_4 + \log\gamma\,\mathrm{AH_2}^{\mathrm{hs}} + \left(\log\gamma\,\mathrm{Fe(CN)_6^{3-}}^{\mathrm{el}} + \log\gamma\,\mathrm{Fe(CN)_6^{3-}}^{\mathrm{hs}}\right) - \left(\log\gamma\,\mathrm{AC^{\ddagger}}^{\mathrm{el}} + \log\gamma\,\mathrm{AC^{\ddagger}}^{\mathrm{hs}}\right)$

[a] C_1–C_4 are fitting parameters associated with the respective models.

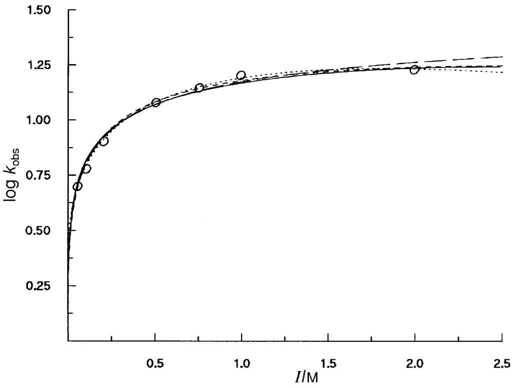

Fig. 1 Ionic strength dependence of log k_{obs} for the oxidation of L-ascorbic acid by hexacyanoferrate(III) according to equations given in Table 2: (——) MSA; (—–) Debye–Hückel; (- - - - - -) Debye–Hückel + linear term; (....) f^{γ}(Pitzer) + linear term. Experimental conditions: $[\mathrm{Fe(CN)_6}^{3-}] = 2.49 \times 10^{-4}$ M, $[\mathrm{H_2A}]_t = 4.97 \times 10^{-3}$ M, pH < 2 and $T = 25$ °C

Figure 1 shows the experimental data and the corresponding plots for the different fitting equations of Table 2. As can be seen, a highly satisfactory fit is obtained when MSA is applied taking the diameters given in Table 1. All these diameters were taken from the literature[16,17] except that of the activate complex (AC‡), which was optimized. All approaches, except the Debye–Hückel approach, seem to fit the experimental results satisfactorily.

MESV thanks Xunta de Galicia for financial support received through Project XUGA 10310B97.

Received, 6th March 1998; Accepted, 27th May 1998
Paper E/8/01853G

References

1 S. P. Mushran, M. C. Agrawal, R. M. Mehrotra and R. Sanehi, *J. Chem. Soc., Dalton Trans.*, 1974, 1960.
2 E. Pelizzeti, E. Mentasti and E. Pramauro, *Inorg. Chem.*, 1978, **17**, 1181.
3 B. Bänsch, P. Martínez, P. Zuluaga, D. Uribe and R. van Eldick, *Inorg. Chem.*, 1991, **30**, 4555.
4 K. W. Watkins and J. A. Olson, *J. Chem. Educ.*, 1980, **57**, 158.
5 L. J. Martins and J. Barbosa da Costa, *J. Chem. Educ.*, 1988, **65**, 176.
6 J. A. Nobrega and F. R. P. Rocha, *J. Chem. Educ.*, 1997, **74**, 560.
7 R. J. Smile, in *Physical Chemistry. Methods, Techniques and Experiments*, Saunders College Pub., Philadelphia, PA, 1990, 630.
8 K. S. Pitzer, in *Activity Coefficients in Electrolyte Solution*, ed. K. S. Pitzer, CRC Press, Boca Raton, FL, 1991, 2nd edn., ch. 3.
9 M. E. Sastre de Vicente, *Curr. Top. Solution Chem.*, 1997, **2**, 157.
10 T. Vilariño and M. E. Sastre de Vicente, *J. Phys. Chem.*, 1996, **100**, 16378.
11 T. Vilariño, S. Fiol, I. Brandariz, X. L. Armesto and M. E. Sastre de Vicente, *J. Chem. Soc., Faraday Trans.*, 1997, **93**, 413.
12 T. Vilariño and M. E. Sastre de Vicente, *J. Solution Chem.*, 1997, **26**, 833.
13 M. E. Sastre de Vicente, T. Vilariño and I. Brandariz, review in *Recent Research Developments in Physical Chemistry*, 1998, in press.
14 A. Haim and M. J. Akhtar, *Inorg. Chem.*, 1988, **27**, 1608.
15 H. L. Friedman, in *A Course in Statistical Mechanics*, Prentice Hall, Englewood Cliffs, NJ, 1985, ch. 7.
16 T. Sun, J. L. Lénard and A. Teja, *J. Phys. Chem.*, 1994, **98**, 6870.
17 B. Bäusch, P. Martinez, J. Zuluaga, D. Uribe and R. van Eldin, *Z. Phys. Chem.*, 1991, **170**, 59.