Mechanistic aspects of nitrate ion reduction on silver electrode: estimation of $O–NO_2^-$ bond dissociation energy using cyclic voltammetry

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Voltammetric investigations of mechanistic aspects and estimation of thermo-chemical parameters of nitrate ion reduction at silver electrode, in alkaline medium are reported. The activation barrier determined from cyclic voltammetry fits a quadratic relation rather than the expected Butler-Volmer kinetics. Intrinsic barrier calculations show that the reduction of nitrate ion on silver follows a concerted mechanism, involving electron transfer initiated bond cleavage, followed by chemical reaction. The bond dissociation energy for the $O–NO_2^-$ bond was estimated to be 48.40 kcal mol^{-1}, which matches well with the reported value of 47.5 kcal mol^{-1}, determined from photodissociation experiments.

1. Introduction

The high water solubility of nitrate ions is responsible for its virtual presence everywhere. Serious clinical symptoms have been reported to be caused by their ingestion,[1–3] which necessitates effective monitoring and development of sensing tools for this ion. For its detection and estimation, a series of methods have been proposed in refs. 4–8. Among them, the electrochemical methods have proved to be advantageous in terms of reproducibility, accuracy, time response and durability.[9] The voltammetric detection is based on the irreversible two-electron transfer process shown in eqn (1):[10]

$$O–NO_2^- + 2e + H_2O \rightarrow NO_2^- + 2OH^- \qquad (1)$$

Using conventional voltammetry,[11,12] in combination with electrochemical scanning tunneling microscopy, surface enhanced Raman spectroscopy,[13] and differential electrochemical mass spectrometry,[14] it is reported that the nitrate ion reduction is very sensitive to the solution conditions, pH and the nature of the electrode material. For example, on polycrystalline platinum electrode, it proceeds through a dissociative adsorption pathway,[15] albeit with slow kinetics. Similar results have been also reported for palladium electrodes,[16] while on Cu, the reduction is found to be very facile and proceeds through the formation of NO_2^- in alkaline medium.[13] Dima *et al.*[14] have reported varying activity of transition and coinage metals and proposed a probable general scheme for the nitrate ion reduction process. In general, nitrate reduction is understood to be a multistep process with the first electron transfer as the rate determining step.[12–14] Among all the metals studied, silver shows highest sensitivity for nitrate ion reduction, and is thus strongly advocated for their electrochemical sensing.[10,17,18] For better understanding and development of Ag as a nitrate ion sensor, it is of utmost importance to have knowledge about the mechanism of this reduction—especially with respect to the rate determining step. To our knowledge, these aspects have not been considered so far. Thus, it was of our immense interest to study the mechanism of this reaction on Ag-electrode, voltammetrically. With this aim, the kinetic investigations of nitrate ion reduction in alkaline media were undertaken through cyclic voltammetry. Our analysis for the first time revealed that the nitrate ion reduction on Ag follows a dissociative electron transfer mechanism. Besides, the related calculations led to the quantification of thermo-chemical parameters, such as bond dissociation energy of the $O–NO_2^-$ bond, which is otherwise estimated through thermal- and photo-dissociation measurements.[19]

2. Experimental

Potassium nitrate and sodium hydroxide were purchased from Merck. Ag-bulk electrode was prepared by sealing a 2 mm diameter Ag (99.9%) wire in a glass tube, with the help of epoxy adhesive. The electrode surface was exposed by grinding it on emery paper. It was polished with commercially available silver cleaner, followed by 0.2 μm alumina powder. Ag/AgCl, KCl (3.0 M), and a Pt rod from Metrohm devices were used as reference and counter electrodes, respectively. Cyclic voltammetric (CV) investigations were performed using Metrohm PGSTAT 100 POTENTIOSTAT/GALVANOSTAT in a three-electrode setup. All the measurements were performed under an argon atmosphere. Prior to measurements, the Ag electrode was electrochemically activated by cycling the potential twenty times (scan rate 1 V s^{-1}) in the potential range −1.3 to 1.0 V, followed by ten potential steps (of 1 s duration) in increasing order of potential, ranging from

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−0.25 to 0.9 V in 2.0 M NaOH. CVs used for analysis were background corrected for the charging current. In view of the reported complications observed during nitrate ion reduction at Ag-electrode,[17] every scan used for the analysis was recorded on a freshly polished and electrochemically cleaned electrode surface. All the measurements were carried out in thermostatted condition at 298 ± 0.1 K.

3. Results and discussion

A typical CV recorded using the Ag electrode in 10 mM KNO_3 and 2 M NaOH (pH = 12) at the scan rate of 10 mV s^{-1} is shown in Fig. 1. High pH helps to shift hydrogen evolution towards more negative potential in comparison to the nitrate ion reduction. A cathodic peak at −0.94 V is assigned to the reduction of nitrate ions. The linear relationship between i_p and the square root of scan rate ($\nu^{1/2}$) (Fig. 1, inset) indicates that the process is diffusion controlled.[20] The scan rate dependent shift in peak potential (E_p), as shown in Fig. 2, is attributed to the irreversibility in the electron transfer process. The magnitude of $E_p - E_{p/2}$ was in the range 47 to 96 mV, which is an indication of electron transfer being the rate determining step.[21] Interestingly, $i_p/\nu^{1/2}$ (Fig. 3) and $E_p - E_{p/2}$ (Table 1) were found to be scan rate dependent. Additionally, peak broadening with increase in scan rate is observed (Fig. 2). *Prima facie*, both these observations could be attributed to the uncompensated *iR* drop and charging current contributions. However, the electrolyte used was highly conducting and moreover, we had subtracted background charging current. Therefore, the contributions of *iR* drop and the capacitance are ruled out. Thus, the shift in the potential and $E_p - E_{p/2}$ with the scan rate are attributed to the potential dependent electron transfer coefficient (α) for the reaction[22] and nitrate ion reduction does not follow a normal Butler–Volmer kinetics. Since the i_p *vs.* $\nu^{1/2}$ plot shows that the process is diffusion controlled, it also suggests that the potential dependent free energy of activation for the reaction is a quadratic function of electrode potential, as per eqn (2):[23]

$$\Delta G^{\ddagger} = \Delta G_o^{\ddagger}\left(1 + \frac{\Delta G^o}{4\Delta G_o^{\ddagger}}\right)^2 \qquad (2)$$

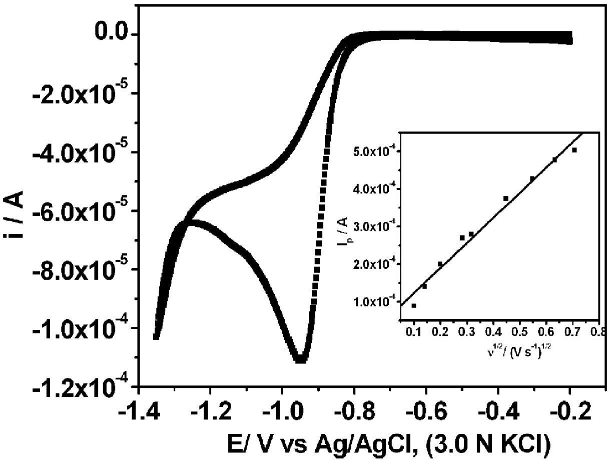

Fig. 1 Typical cyclic voltammogram recorded on Ag electrode in 10 mM KNO_3 and 2 M NaOH, at a scan rate of 10 mV s^{-1}. Inset shows a linear fit of the peak current (i_p) *vs.* square root of scan rate ($\nu^{1/2}$), which indicates diffusion controlled reaction.

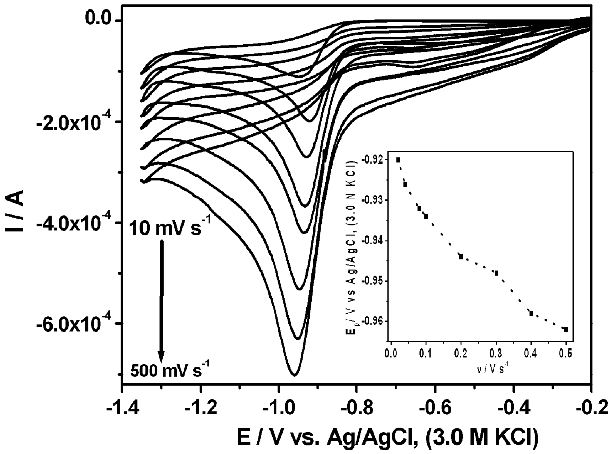

Fig. 2 Cyclic voltammograms recorded on Ag electrode in 10 mM KNO_3 and 2 M NaOH, at varying scan rates from 10 to 500 mV s^{-1}. Inset shows peak potential *vs.* scan rate, which indicates that the reduction is irreversible.

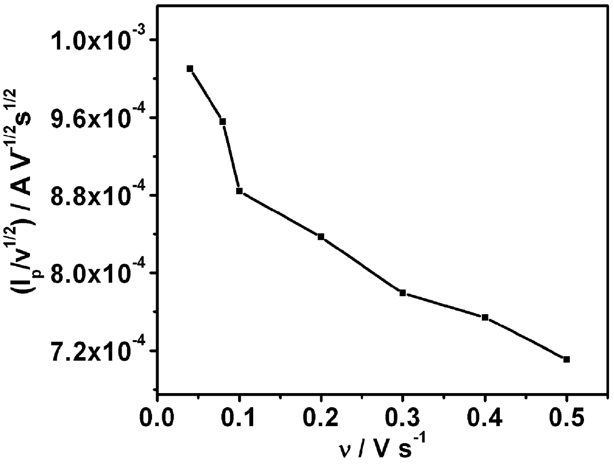

Fig. 3 $i_p/\nu^{1/2}$ *vs.* scan rate for NO_3 reduction on Ag electrode in alkaline medium, indicating a deviation from Butler-Volmer kinetics.

Table 1 Analysis of cyclic voltammetric (CV) data obtained for nitrate ion reduction (10 mM) at an Ag electrode in 2 M NaOH at 298 K

Scan rate/V s^{-1}	$10^4 I_p$/A	E_p/V	($E_p - E_{p/2}$)/V	$\Delta G_o^{\ddagger}$/ kcal mol^{-1}
0.01	0.891	−0.944	0.060	19.97
0.02	1.40	−0.920	0.065	19.56
0.04	2.01	−0.926	0.072	19.66
0.08	2.70	−0.932	0.078	19.77
0.1	2.80	−0.934	0.083	19.80
0.2	3.74	−0.944	0.085	19.97
0.3	4.27	−0.948	0.087	20.04
0.4	4.77	−0.958	0.089	20.22
0.5	5.03	−0.962	0.094	20.28

where,

$$\Delta G^{o} = F(E - E^{o\prime}) \tag{3}$$

in which $E^{o\prime}$ is the formal potential for overall reaction and has a value of 0.01 V[24] and $\Delta G_o^{\ddagger}$, is the intrinsic energy barrier for the reduction reaction.

The potential dependent rate constant ($k(E)$) is given by eqn (4):

$$k(E) = Z.\exp\left[\frac{-\Delta G^{\ddagger}}{RT}\right] \tag{4}$$

where, $Z\ (= (RT/2\pi M)^{1/2}$, M is the molecular mass of NO_3^-) = 2521.79 cm s^{-1}.

Such dissociative redox reactions initiated with electron transfer can occur through two plausible mechanisms, namely stepwise (eqn (5) and (6)) and concerted (eqn (7)):

$$\mathrm{A{-}B} + e^- \rightarrow \mathrm{A{-}B}^{\bullet -} \tag{5}$$

$$\mathrm{A{-}B}^{\bullet -} \rightarrow \mathrm{A}^{\bullet}{-}\mathrm{B}^- \tag{6}$$

$$\mathrm{A{-}B} + e^- \rightarrow \mathrm{A}^{\bullet} + \mathrm{B}^- \tag{7}$$

Products formed through both these mechanisms can undergo further electron transfer or chemical reactions, which affect the thermodynamic and kinetic aspects of the overall process. Theory as well as experimental predictions associated with these mechanisms for alkyl halides,[25] peroxides[22,26] and other analytes[27,28] have been well documented in the literature. The two mechanisms can be differentiated on the basis of difference in the value of intrinsic energy barrier, as given below (eqn (8) and (9)):

$$\Delta G_o^{\ddagger}(\text{stepwise}) = \frac{\lambda_0 + \lambda_i}{4} \tag{8}$$

$$\Delta G_o^{\ddagger}(\text{concerted}) = \frac{\lambda_0 + \lambda_i + \mathrm{BDFE}}{4} \tag{9}$$

where, BDFE is the bond dissociation free energy, and λ_0, the solvent reorganization energy, which is calculated through the Marcus equation (10):

$$\lambda_0 = \frac{e}{8\pi\varepsilon_o a_o}\left(\frac{1}{\varepsilon_o} - \frac{1}{\varepsilon_s}\right) \tag{10}$$

Here, ε_o and ε_s are the optical and static dielectric constants of the solvent, respectively and a_o, the effective radius of the analyte, which is calculated using eqn (11):

$$a_o = a_B\left(\frac{2a_{AB} - a_B}{a_{AB}}\right) \tag{11}$$

where $a_{AB} = a_{NO_3^-} = 2.64$ Å and $a_B = a_{O^-} = 1.76$ Å are as reported previously.[29] λ_i is regarded as the internal reorganization energy and can be neglected due to its comparatively small magnitude. λ_0 was calculated using reported values for optical and static dielectric constants for water.[30] Use of convolutive analysis of CVs has been reported for the calculation of intrinsic barriers and other mechanistic details of such electron transfer reactions. Though, the method has many advantages, its use is limited due to the requirement of information regarding the double layer structure. Except for mercury, such information is not available for other metal electrodes. We used another simple approach for calculation of the barrier using cyclic voltammetry, without any convolution analysis, which is as follows.

The free energy of activation at peak potentials obtained in cyclic voltammograms is given by eqn (12):[31]

$$\Delta G_P^{\ddagger} = \frac{RT}{F}\left[\ln\left(Z\sqrt{\frac{RT}{F\alpha\nu D}}\right) - 0.78\right] \tag{12}$$

Knowing the value of α calculated from $E_p - E_{p/2}$, where E_p is the peak potential and $E_{p/2}$ is the potential where the current is at half the peak value (Table 1), through eqn (13):[20]

$$\alpha = \left(\frac{1.86RT}{F|E_p - E_{p/2}|}\right) \tag{13}$$

and D (1.9×10^{-5} cm^2 s^{-1}), $\Delta G_P^{\ddagger}$ values for the various scan rates were calculated. These values were substituted in eqn (2) and the resulting quadratic equation was solved for $\Delta G_o^{\ddagger}$ with the help of the FORTRAN program, written specifically for this purpose. Among the two roots obtained, the negative root was not considered as the value emerged out to be less than that obtained from eqn (8), which is the bare minimum value expected for the overall reaction. The positive root, gives a value of $\Delta G_o^{\ddagger}$ much greater than that expected for a stepwise mechanism (eqn (5) and (6)) and hence negating the possibility that the reduction follows a stepwise mechanism. Therefore, the reaction occurring through the concerted mechanism as shown in eqn (7) is inferred. Preference of a concerted mechanism over a stepwise one is also realized by considering the resonance structure of nitrate ion and the nitrite ion as against the open shell structure of $NO_3^{\bullet 2-}$—an intermediate which would be formed in a stepwise mechanism.

The bond dissociation energy was calculated by substituting the value of $\Delta G_o^{\ddagger}$ (from the above procedure) and λ_o (from eqn (10)) in eqn (9) and found to be *ca.* 48.4 kcal mol^{-1}, which matches well with the value of 47.5 kcal mol^{-1}, reported from photodissociation measurements.[19] The small difference is attributed to the neglecting the value of λ_i in the calculations as a first approximation.

Based on our experimental findings and earlier reports,[13,14,32,33] we conclude that, electron transfer to the nitrate ion is the rate determining step, similar to the process reported for Cu, and following the overall reaction scheme given by eqn (14) and (15):

$$NO_3^- + e^- \rightarrow NO_2^- + O^{\bullet -}\ \text{(rate determining step)} \tag{14}$$

$$O^{\bullet -} + e^- + H_2O \rightarrow 2OH^- \tag{15}$$

Results published recently by Broder *et al.*[34] also suggest the formation of $O^{\bullet -}$ as an intermediate in reduction of nitrate ion at Pt electrode in room-temperature ionic liquids.

4. Conclusion

For the first time, we have used a simple procedure for analyzing the cyclic voltammetric data for nitrate ion reduction at a silver electrode. Data fits very well in the dissociative electron transfer concerted mechanism. Besides, the value of the bond dissociation energy, *ca.* 48.4 kcal mol^{-1}, calculated from these investigations, matches with 47.5 kcal mol^{-1} the value obtained from photodissociation measurements. This knowledge of mechanistic and thermo-chemical parameters is believed to be useful in designing Ag electrodes as nitrate ion sensors.

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References

1 G. Ellis, I. Adatia, M. Yazdanpanah and S. K. Makela, *Clin. Biochem.*, 1998, **31**, 195.
2 C. S. Bruning-Fann and J. B. Kaneene, *Vet. Hum. Toxicol.*, 1993, **35**, 237.
3 National Research Council, *Ground Water Vulnerability Assessment, Predicting relative contamination potential under conditions of uncertainty*, National Academy Press, Washington DC, 1993, p. 14.
4 M. A. Ferree and R. D. Shannon, *Water Res.*, 2001, **35**, 327.
5 S. Kage, K. Kudo and N. Ikeda, *J. Chromatogr. B: Biomed. Appl.*, 2000, **742**, 363.
6 J. A. Morales, L. S. de Graterol and J. Mesa, *J. Chromatogr. A*, 2000, **884**, 185.
7 V. Jedlickova, Z. Paluch and S. Alusik, *J. Chromatogr. B: Anal. Technol. Biomed. Life Sci.*, 2002, **780**, 193.
8 T. Miyado, Y. Tanaka, H. Nagai, S. Takeda, K. Saito, K. Fukushi, Y. Yoshida, S. Wakida and E. Niki, *J. Chromatogr. A*, 2004, **1051**, 185.
9 M. J. Moorcroft, J. Davis and R. G. Compton, *Talanta*, 2001, **54**, 785.
10 J. Krista, M. Kopanica and L. Novotny, *Electroanalysis*, 2000, **12**, 199.
11 K. Bouzek, M. Paidar, A. Sadilkova and H. Bergmann, *J. Appl. Electrochem.*, 2001, **31**, 1185.
12 J. Davis, M. J. Moorcroft, S. J. Wilkins, R. G. Compton and M. F. Cardosi, *Analyst*, 2000, **125**, 737.
13 S.-E. Bae, K. L. Stewart and A. A. Gewirth, *J. Am. Chem. Soc.*, 2007, **129**, 10171.
14 G. E. Dima, A. C. A. de Vooys and M. T. M. Koper, *J. Electroanal. Chem.*, 2003, **554**, 15.
15 M. C. P. M. da cunha, M. Weber and F. C. Nart, *J. Electroanal. Chem.*, 1996, **414**, 163.
16 M. Wasberg and G. Horanyi, *Electrochim. Acta*, 1995, **40**, 615.
17 D. Kim, I. B. Goldberg and J. W. Judy, *Analyst*, 2007, **132**, 350.
18 M. Fedurco, P. Kedzierzawski and J. Augustynski, *J. Electrochem. Soc.*, 1999, **146**, 2569.
19 B. Kim, PhD Thesis, University of California, USA, 1991.
20 A. J. Bard and L. R. Faulkner, *Electrochemical Methods: Fundamentals and Applications*, Wiley, New York, 2nd edn, 2001.
21 C. P. Andrieux and J. M. Saveant, in *Investigations of Rates and Mechanisms of Reactions*, ed. C. F. Bernasconi, Wiley, New York, 1986, part 2, vol. VI/4E.
22 S. Antonello, M. Musumeci, D. D. M. Wayney and F. Maran, *J. Am. Chem. Soc.*, 1997, **119**, 9541.
23 J. M. Saveant, in *Advances in Electrontransfer Reactions*, ed. P. S. Mariano, JAI Press, Greenwich, 1994, vol. 4, p. 53.
24 *Handbook of Electrochemistry*, ed. C. G. Zoski, Elsevier, Amsterdam, 1st edn, 2007.
25 J. M. Saveant, *J. Am. Chem. Soc.*, 1987, **109**, 6788.
26 S. Antonello and F. Maran, *J. Am. Chem. Soc.*, 1999, **121**, 9668.
27 A. Cardinale, A. A. Isse, A. Gennaro, M. Robert and J. M. Saveant, *J. Am. Chem. Soc.*, 2002, **124**, 13533.
28 R. L. Donkers and M. S. Workentin, *J. Phys. Chem. B*, 1998, **102**, 4061.
29 *Handbook of Chemistry and Physics*, CRC Press, New York, 80th edn, 1999–2000.
30 J. A. Riddick and W. B. Bunger, in *Organic Solvents: Physical Properties and Methods of Purification*, John Wiley and Sons, New York, 3rd edn, 1970, vol. II.
31 L. Pause, M. Robert and J. M. Saveant, *J. Am. Chem. Soc.*, 2000, **122**, 9829.
32 O. M. Magnussen, *Chem. Rev.*, 2002, **102**, 679.
33 M. Kleinert, A. Cuesta, L. A. Kibler and D. M. Kolb, *Surf. Sci.*, 1999, **430**, L521.
34 T. L. Broder, D. S. Silvester, L. Aldous, C. Hardacre, A. Crossley and R. G. Compton, *New J. Chem.*, 2007, **31**, 966.