

LETTERS

Electroreduction of Nitromethane in Aqueous Solution. A Surface Indifferent Electrocatalytic Reaction

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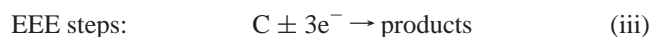
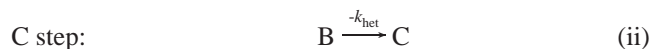
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The electroreduction of nitromethane in aqueous solution is shown to follow a mechanism of the heterogeneous ECEEE type on gold electrodes as also seen for platinum and other substrates. Moreover, the rate of the chemical step is surprisingly similar, to within less than an order of magnitude, on all surfaces studied. Kinetic isotope measurements show that the chemical step in the reaction sequence is approximately a factor of 2 slower in D₂O than in H₂O. A mechanism is proposed that accounts for the lack of surface sensitivity and for the observed isotope effect.

1. Introduction

Nitromethane can be electrochemically reduced in aqueous solution at a variety of electrode materials to give the corresponding hydroxylamine in a reaction that involves the uptake of four electrons and four protons in addition to the cleavage of a N—O bond.^{1–5} Clearly for such a reaction a large variety of candidate electrode reaction mechanisms present themselves! Nevertheless impedance voltammetry,^{6–9} hydrodynamic voltammetry,^{10–12} and spectroelectrochemical methods¹⁰ have all indicated that the reaction proceeds via an ECEEE mechanism of the general type



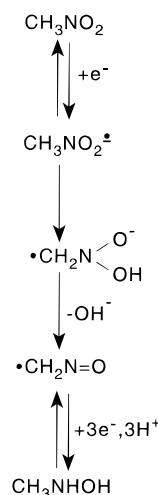
where the rate-determining chemical step has been shown to

be heterogeneous and where the net current flowing is given by an expression of the form

$$I = F \int \left(D \frac{\partial [\text{A}]}{\partial y} + 3k_{\text{het}}[\text{B}] \right)_{y=0} \text{d}A \quad (1)$$

where F is the Faraday constant, y is a coordinate normal to the electrode surface, and the integration is over the surface area, A , of the electrode. The specific details of the mechanism as thought to apply to the nitromethane reduction are shown in Scheme 1.^{6–12} This mechanism has been shown to apply to a diversity of electrode materials including platinum,¹² Hg/Cu,¹¹ and Hg/Au.¹⁰ In all of these cases it has been possible to measure a value for the heterogeneous rate constant, k_{het} , describing the chemical step in the reaction. For platinum in the pH range 7.0–9.0 this value was $0.26 \pm 0.07 \text{ cm s}^{-1}$. For Hg/Cu it was 0.18 cm s^{-1} , and for Au/Hg 0.06 cm s^{-1} . Consideration of these values shows a surprising independence of the heterogeneous rate constant on the chemical identity of the surface with all the values being similar to within less than an order of magnitude.

SCHEME 1



The work reported in this paper seeks first to examine the reduction of nitromethane at gold electrodes to see if again mechanistic and kinetic similarities appear and second to consider possible reasons for the observed surface indifference of the electrocatalysis. To this latter end kinetic isotope measurements made in D₂O are reported and shown to give useful insight.

2. Experimental Section

A fast flow channel electrode system was employed that could deliver solutions at flow rates of up to ca. 5 cm³ s⁻¹ through a flow cell constructed of silica and having a cross-sectional area of 2 mm × 0.1 mm. Full details of the rig and operating procedures have been described elsewhere.^{11,13} Platinum and gold microband electrodes were fabricated by sealing a strip of metal foil (Goodfellow Metals, Cambridge, U.K.) between two glass rods followed by polishing in the manner reported elsewhere.¹¹ Precise determinations of the area of platinum (40.6 μm × 0.094 cm) or gold (25.0 μm × 0.104 cm) were obtained using either a scanning electron microscope or a Topometrix AFM. The working electrode potential was controlled through a conventional three-electrode potentiostat system with a platinum coil counter electrode located downstream so as to prevent contamination by counter electrode electrolysis products. Potentials were measured relative to a platinum wire quasi-reference electrode. Measurements were made at a temperature of 25 °C.

Aqueous (H₂O) solutions were made up using Elgastat (High Wycombe, U.K.) UHQ grade water of resistivity 18 MΩ cm. D₂O was obtained from Aldrich (99 at. %). Solutions of nitromethane (puriss, absolute, Fluka) or CD₃NO₂ (Aldrich, 99 at. % D) were prepared immediately prior to the experiment and were buffered using buffer solutions based on either 0.2 M KH₂PO₄ (pH 6–7) or 0.2 M boric acid (pH 7.5–9). In all cases the buffers were adjusted to the desired pH by addition of KOH solution and additionally contained 1.0 M KCl (Aldrich, >99%) as supporting electrolyte. Solutions were thoroughly purged of oxygen before use with nitrogen that had been presaturated by prepassage through an identical solution to that being degassed. Flow rates through the channel cell were calibrated separately for H₂O and D₂O.

Data analysis was conducted using a custom-written data analysis program (written in Microsoft Visual C++/MFC running under Windows 3.11, which allowed limiting currents and half-wave potentials to be measured from the voltammo-

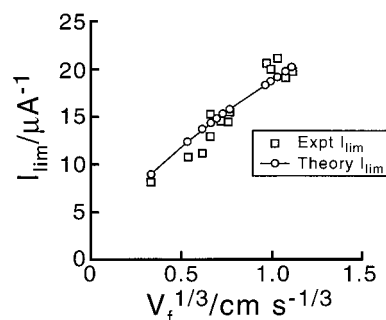


Figure 1. Variation of the transport-limited current with the electrolyte flow rate as measured (□) at a gold microband electrode in buffered aqueous solution (pH 6). The symbols (○) show the behavior simulated for an ECEEE mechanism using a best fit value for k_{het} of 0.095 cm s⁻¹.

grams). Previous work¹⁰ established a value of 2.0×10^{-5} cm² s⁻¹ for the diffusion coefficient of nitromethane in aqueous solution, and this value was used in all modelling of experimental data in H₂O.

Measurements of pH were made using a glass combination electrode (BDH, Poole, Dorset, U.K.) in conjunction with a Jenway 3030 pH meter (Jenway Ltd., Dunmow, Essex, U.K.). When solutions in D₂O were examined in this way, a correction of 0.4 units was made to convert from pH to pD.¹⁴

3. Experimental Results

Experiments were first conducted on the reduction of nitromethane (1.48 mM) in aqueous media in a pH 6 buffer of KH₂PO₄ using a 25 μm gold microband electrode in a fast flow channel electrode capable of delivering volume flow rates in the range 0.03–2.5 cm³ s⁻¹. The recorded voltammograms showed half-wave potentials in the range -0.78 to -0.85 V (vs Pt pseudo-reference electrode). Voltammograms were recorded as a function of flow rate. A typical plot is shown in Figure 1 together with the best fit behavior simulated for an ECEEE process, using theory previously developed,¹¹ by optimizing the value of k_{het} . The approximate linear dependence of the current on the cube root of the flow rate is indicative of the heterogeneous nature of the chemical step.¹¹ The simulated behavior is seen to satisfactorily reproduce the observed behavior, suggesting that an ECEEE mechanism again operates at gold electrodes, and such measurements permitted a mean value of 0.095 ± 0.005 cm s⁻¹ for k_{het} to be inferred. Next mass transport corrected Tafel plots¹² were measured from the experimental voltammograms and values of the Tafel slope at the halfwave potential

$$\left[\frac{dE}{d(\log_e[I^{-1} - I_{\text{lim}}^{-1}])} \right]_{E=E_{1/2}} \quad (2)$$

were interpreted either in terms of a simple n -electron transfer process or via theory generated for a heterogeneous ECEEE reaction.¹² In the former case a systematic variation of the standard electrochemical rate constant, k_0 , for the CH₃NO₂/[CH₃-NO₂]^{•-} couple with electrolyte flow rate was observed as shown in Figure 2., whereas for the latter analysis, using the value of k_{het} inferred above, the deduced values were independent of the mass transport rate (Figure 2). This provides strong additional and independent evidence for the operation of an ECEEE mechanism on gold and for the veracity of the heterogeneous rate constant, k_{het} .

A mean value of 0.196 ± 0.001 cm s⁻¹ was inferred for the electrochemical rate constant. That this is in close agreement

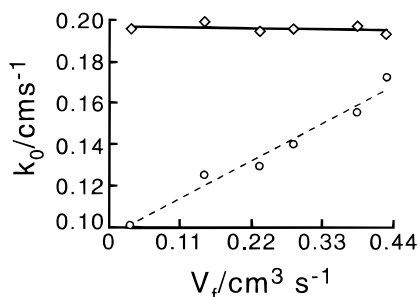


Figure 2. Variation of the standard electrochemical rate constant, k_0 , with electrolyte flow rate as determined from Tafel slopes interpreted either in terms of a simple E process (---) or in terms of an ECEEE process (—) using the value of k_{het} determined via analysis of the transport-limited current.

with values analogously inferred from data recorded at platinum electrodes¹² is consistent with the mechanistic scenario proposed in which the $\text{CH}_3\text{NO}_2/[\text{CH}_3\text{NO}_2]^{\bullet-}$ reduction results from outer-sphere electron transfer with the electrode.

The above analysis confirms that nitromethane reduction on gold, as found with platinum, mercury, Hg/Cu, and Hg/Au, follows an ECEEE mechanism and that the value of the rate constant for the apparently heterogeneous chemical step is again close to 0.1 cm s^{-1} . To glean further mechanistic insight with a view to understanding these similarities of behavior, experiments were next conducted using a platinum microband electrode to study the electroreduction of CD_3NO_2 in D_2O .

The electroreduction of nitromethane (3.7 mM) in D_2O solutions of pD 8.9 and 9.4 was examined using a $40 \mu\text{m}$ platinum microband electrode. Voltammograms showed half-wave potentials in the range -0.95 to -1.10 V (vs Pt) with no systematic variation with pD. In particular the transport-limited current was investigated as a function of the rate of mass transport. Again an approximate cube root dependence on flow rate was observed, which could be accurately simulated using the theory for a heterogeneous ECEEE reaction. The magnitude of the currents flowing in D_2O were significantly less than those seen under corresponding conditions in H_2O solvent suggesting a significant kinetic isotope effect on the electrode reaction.

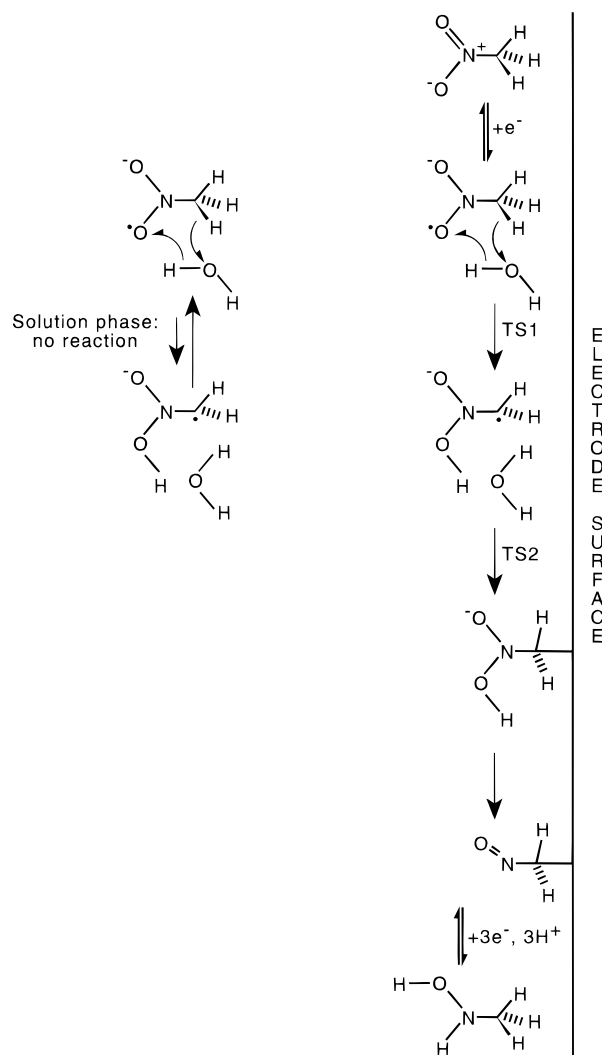
In order to quantify any isotope effect on k_{het} , it was necessary to know the value of the diffusion coefficient, D , of nitromethane in both H_2O and D_2O . In the former a value of $2 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ has been established.¹⁰ The corresponding value in D_2O may be reliably estimated¹⁵ on the basis of the Stokes–Einstein equation relating the diffusion coefficient to the solvent viscosity, η

$$D_{\text{D}_2\text{O}} = D_{\text{H}_2\text{O}} \frac{\eta_{\text{H}_2\text{O}}}{\eta_{\text{D}_2\text{O}}} \quad (3)$$

It follows that, neglecting the effects of deuteration of the substrate CH_3NO_2 , a value of $1.6 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ can be estimated for the diffusion coefficient of CH_3NO_2 or CD_3NO_2 in D_2O using tabulated known values for η .

Knowledge of the diffusion coefficient for nitromethane in D_2O permitted the quantitative modeling of transport-limited current data to find values of k_{het} for comparison with data obtained in H_2O .¹² Analysis, analogous to that used to generate Figure 1, resulted in the following values of k_{het} in D_2O : 0.12 cm s^{-1} (pD 8.9), 0.13 cm s^{-1} (pD 9.4). These may be compared with values of 0.24 cm s^{-1} (pH 8.5) and 0.28 (pH 9.0) found in H_2O .¹² It is evident that a significant isotope effect operates for the electroreduction on platinum with the chemical step being two or more times slower in deuterated solution.

SCHEME 2



4. Discussion

All the mechanistic evidence concerning the electroreduction of nitromethane in aqueous solution suggests that the reaction follows an ECEEE type process with the chemical step only proceeding on the electrode surface. Consistent with this in situ electrochemical ESR experiments revealed both the presence of the $[\text{CH}_3\text{NO}_2]^{\bullet-}$ radical anion during reduction of nitromethane at Hg/Au electrodes and the fact that in homogeneous solution the species was stable on the voltammetric time scale with loss of the radical ion only being observed at the electrode surface. The heterogeneous nature of the kinetic decay is also evident from impedance data^{6–9} and is particularly clear from hydrodynamic voltammetry^{10–12} where the dependence of the transport-limited current on the rate of mass transport is quite different from that expected for a coupled homogeneous chemical reaction.¹¹ Nevertheless if the reaction is heterogeneous it must occur in such a manner that the chemical nature of the electrode surface exerts rather little influence on the overall kinetics of the reaction.

Consistent with the observation of surface indifference, and taking into account the significant isotope effect measured between H_2O and D_2O , we propose that the transition state for the reaction involves the transfer of H^{\bullet} (or D^{\bullet}) from carbon to oxygen as shown in Scheme 2. In homogeneous solution this occurs only very slowly so that the anion radical $[\text{CH}_3\text{NO}_2]^{\bullet-}$ is stable on the voltammetric time scale. However, if the

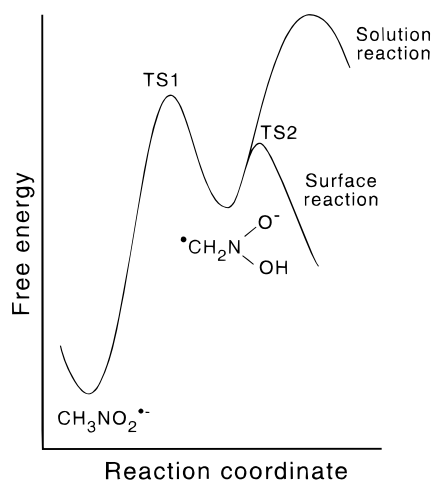


Figure 3. Schematic reaction profile showed the proposed mechanism for the electroreduction of nitromethane.

reaction occurs in solution but adjacent to the electrode surface then the species $\bullet\text{CH}_2\text{N}(\text{OH})\text{O}^-$ may adsorb onto the electrode surface so ensuring the irreversibility of the chemical step. Of course if the energy barrier to adsorption is less than that required for the H (D) atom transfer then the reaction rate will be insensitive to the former and hence to the chemical identity of the electrode surface. The schematic reaction profile shown in Figure 3 summarizes the proposed mechanism. The slow step in the electrode reaction corresponds to transition state TS1 with the transition state for adsorption, TS2, being of lower energy, at least for the electrode materials studied hitherto. In contrast, for homogeneous solution the transition state corresponding to further reaction of $\bullet\text{CH}_2\text{N}(\text{OH})\text{O}^-$ is of higher energy than TS1 so that $\bullet\text{CH}_2\text{N}(\text{OH})\text{O}^-$ is then unstable with respect to reconversion to the radical anion $[\text{CH}_3\text{NO}_2]^{*-}$ so explaining the observed relative stability of the latter in the absence of an adsorbing surface.

It is useful to note that the observed "heterogeneous" kinetics inferred voltammetrically and summarized by eq 1 are consistent first with a conventional heterogeneous reaction in which there is adsorption of the intermediate, B, formed in reaction (ii)



before conversion into species C



and further electrochemical and chemical reaction. In this case the net rate constant

$$k_{\text{het}} = K_{(\text{iv})}k_{(\text{v})} \quad (4)$$

reflecting both the adsorption constant, $K_{(\text{iv})}$, for reaction iv and the heterogeneous rate constant, $k_{(\text{v})}$, for reaction v. Second,

the kinetic formulation is also compatible with the mechanism proposed above for nitromethane in which the slow chemical reaction (ii) in the ECEEE pathway occurs in homogeneously in the layer of solution immediately adjacent to the electrode solution



followed by irreversible adsorption of the species C



and subsequent irreversible transformation leading to a flow of current beyond that expected for a simple one-electron process. In this case k_{het} simply reflects the rate of step vi. It follows that a voltammetrically inferred current behavior given by eq 1 does not in itself indicate that the rate-determining step occurs on the electrode surface.

Returning to the case of the nitromethane reduction, we note that the mechanism proposed in Scheme 2 is consistent with *all* the presently known experimental data relating to the reaction at a diversity of electrode surfaces and that the surface indifference of the reaction can be explained by a homogeneous chemical transformation of the $[\text{CH}_3\text{NO}_2]^{*-}$ radical anion occurring in an electrode reaction layer and which is rendered irreversible, and so kinetically visible, by adsorption onto any suitable electrode surface.

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