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Chemistry of Electron Transfer and Oxygen Transfer in Fused Salts[1]

Sir:

The oxygen electrode in molten alkali nitrate solvents has been the subject of significant controversies.[2-6] Recently, Inman[7] has reported (at an $O_2(Au)|O^{2-}$ electrode in a lithium–potassium chloride eutectic melt at 450°) a puzzling Nernstian slope of RT/F, in lieu of the expected $RT/2F$ for $2O^{2-} = O_2 + 4e$. We have substantiated polarographically a similar remarkable finding at Levich's rotated platinum disk electrode,[8] in solutions prepared by adding pure sodium oxide to a fused equimolar sodium–potassium nitrate solvent at 265°. Our results indicate conclusively the prevalence of the following oxygen-transfer (I) and electron-transfer (II) processes.

Oxygen transfer

$$NO_3^- + O^{2-} \longrightarrow NO_2^- + O_2^{2-} \qquad (I_1)$$

$$2NO_3^- + O_2^{2-} \rightleftharpoons 2NO_2^- + 2O_2^- \qquad (I_2)$$

Electron transfer

$$NO_2^- \rightleftharpoons NO_2 + e \qquad (II_1)$$

$$O_2^- \rightleftharpoons O_2 + e \qquad (II_2)$$

$$O_2^{2-} \rightleftharpoons O_2^- + e \qquad (II_3)$$

Because of reaction I_1, the ion O^{2-} cannot exist (at any appreciable concentration level) in equilibrium with nitrate melts. This is plausible in view of indications that in such media NO_3^- indeed exhibits the properties of a strong and reactive oxidant.[9]

The evidence on which our claim for the proposed reaction sequence rests is summarized in Figure 1 which is representative of an extensive series of experiments.

The steady-state current–voltage (c–v) curve shown in Figure 1 exhibits several sigmoid "waves," reminiscent of the shape of classical polarograms. Four well-defined limiting current domains (i) are evident. Their dependence on the angular velocity (ω) of the rotated disk indicator electrode was found to obey Levich's[8] applicable equations

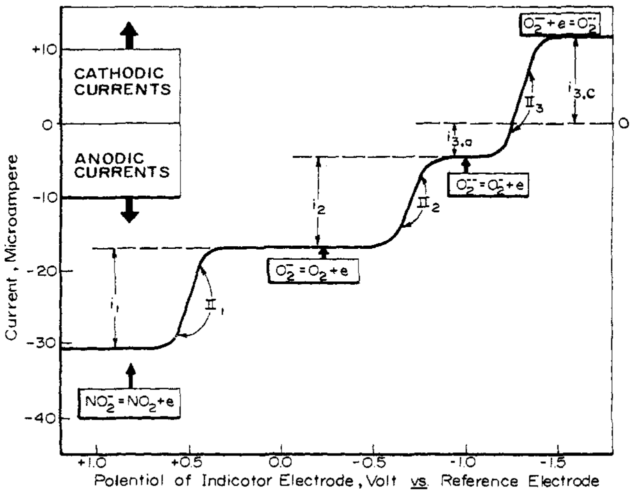

Figure 1. Typical current–voltage curve (corrected for residual currents, etc.) recorded at 265° in platinum-lined electrolysis cell: electrolyte, equimolar sodium–potassium nitrate, equilibrated with sodium oxide (1.10 mmoles of Na_2O per 1000 g of solvent); supernatant atmosphere, dry argon; indicator electrode, Levich's platinum disk, rotated at 600 rpm; reference electrode, $Ag|AgNO_3$(0.07 *m* in solvent melt). Potentials assigned in accordance with the Stockholm IUPAC Convention.

$$i = (\text{constant})D^{2/3}\omega^{1/2}C \qquad (III)$$

$$i/D^{2/3} \propto C\,(\text{when } \omega = \text{constant}) \qquad (IV)$$

where D and C denote respectively the diffusion coefficient and bulk concentration of the electroreactive (electrooxidizable or electroreducible) species. This concordance is an unequivocal diagnostic criterion indicating that our experimentally observed limiting currents were controlled by the rate of transport of the electroreactive species from the bulk of the melt to the electrode surface, under conditions of extreme concentration polarization.

The anodic wave designated as II_1 in Figure 1 is readily identifiable in terms of its known half-wave potential and analytic geometry characteristics[3,5,10,11] with the electrooxidation of nitrite to NO_2 in accordance with eq II_1. The limiting current i_1 was proportional to the concentration of the ion NO_2^- in the bulk of the melt, as required by eq IV. We postulate the correspondence shown in Figure 1 between the other two c–v waves, on the one hand, and reactions II_2 (superoxide $\rightleftharpoons$ oxygen) and II_3 (peroxide $\rightleftharpoons$ superoxide) on the other hand. The rationale is outlined below.

II_3 is a composite wave whose anodic and cathodic limiting currents $i_{3,a}$ and $i_{3,c}$ were proportional to the bulk concentrations of peroxide (O_2^{2-}) and superoxide (O_2^-), respectively. The limiting current, i_2, of the anodic wave II_2 was also proportional to superoxide concentration. Quite generally on any given c–v curve

$$|i_{3,c}| = |i_2| \qquad (V)$$

These findings are uniquely consistent with the interpretations presented in Table I. It is apparent from the table that limiting currents i_2 and $i_{3,c}$ were due to the electrooxidation and electroreduction of the same

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(1) Investigation supported by the U. S. Atomic Energy Commission (Report No. NYO-2133-46).

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Table I. Intepretation of Current–Voltage Waves

Current–voltage wave[a]	Applicable limiting current eq[b,c]	Corresponding electrode process
II_2	$-i_2 = (\text{constant}) \cdot D_{O_2^-}{}^{-2/3} C_{O_2^-}$	$O_2^- = O_2 + e$
II_3, cathodic portion	$i_{3,c} = (\text{constant}) \cdot D_{O_2^-}{}^{-2/3} C_{O_2^-}$	$O_2^- + e = O_2^{2-}$
II_3, anodic portion	$-i_{3,a} = (\text{constant}) \cdot D_{O_2^-}{}^{-2/3} C_{O_2^{2-}}$	$O_2^{2-} = O_2^- + e$

[a] Identified in Figure 1. [b] Based on eq IV; D and C denote diffusion coefficients and bulk concentrations, respectively. [c] Cathodic and anodic currents are assigned positive and negative values, respectively.

species (superoxide), both processes involving a one-electron transfer. This accounts for experimental result V. Our data also revealed the following correlation between the "nitrite wave" (II_1), on the one hand, and the superoxide and peroxide waves (II_2 and II_3), on the other hand.

$$|i_1| D_{NO_2^-}{}^{-2/3} = |i_{3,a}| D_{O_2^{9-}}{}^{-2/3} + 1.5|i_2| D_{O_2^-}{}^{-2/3} = |i_{3,a}| D_{O_2^{2-}}{}^{-2/3} + 1.5|i_{3,c}| D_{O_2^-}{}^{-2/3} \quad \text{(VI)}$$

Equation VI is evidently consistent with the stoichiometry inherent in eq I_1 and I_2 (= generation of 1 mole of nitrite per mole of peroxide, and of 1.5 moles of nitrite per mole of superoxide).

Assuming the prevalence of Nernst-controlled electron-transfer equilibria, derivations based on well-known principles of polarographic theory yielded the "wave equations" VII and VIII, where $i(E)$ denotes the current at potential E and $E_{1/2}$ the half-wave potential.

For II_2 at 265°

$$E = E_{1/2} + \frac{2.3RT}{F} \log \frac{i(E)}{i_2 - i(E)} \quad \text{(VII)}$$

For II_3 at 265°

$$E = E_{1/2}' + \frac{2.3RT}{F} \log \frac{i_{3,c} - i(E)}{i(E) - i_{3,a}} \quad \text{(VIII)}$$

The relevant Nernstian slopes determined from our experiments were 0.109 ± 0.002 v for II_2 and 0.106 ± 0.003 v for II_3, which is in good agreement with the theoretical assignment of $(2.3RT/F) = 0.107$ v in eq VII and VIII.

The "oxygen- and electron-transfer chemistry" postulated in equation sequence I–II was further confirmed by the following observations: (a) voltammograms similar to Figure 1 were obtained when sodium peroxide (in lieu of sodium oxide) was equilibrated with the alkali nitrate solvent melt, except that $|i_1|$ was relatively smaller (due to reaction I_2 occurring in the absence of reaction I_1); (b) direct equilibration of the solvent with pure potassium superoxide (in the absence of peroxide, oxide, and nitrite) yielded $i_{3,c} = -i_2$ (in accordance with eq V), but i_1 and $i_{3,a} = 0$.

The reproducibility of the results reported in this communication was critically contingent on the use of platinum-lined electrolysis cells (in order to obviate contact with silica) and on the presence of an inert and dry supernatant atmosphere. Otherwise, side reactions of the type $SiO_2 + O^{2-} = SiO_3{}^{2-}$ and $O^{2-} + H_2O = 2OH^-$ occurred, which may well account for discrepant reports in the literature. Furthermore, we found that bubbling of gaseous oxygen through the melts converted peroxide quantitatively to superoxide ($O_2^{2-} + O_2 \rightarrow 2O_2^-$) engendering a decrease of $i_{3,a}$, accompanied by a concomitant enhancement of both $i_{3,c}$ and i_2; due to this effect, the superoxide generated *via* reaction II_3 did not contribute to i_2.

In the formulation of eq I and II, the customary "chemical shorthand" (as is practiced when writing H^+ in lieu of H_3O^+) was employed, ignoring solvation. However, solvation effects may be important in view of our (*a priori* unexpected) finding that nitrite could coexist with peroxide and superoxide. Further pertinent work is in progress.

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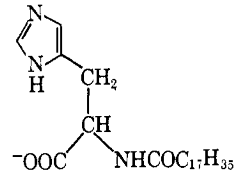
Acceleration of *p*-Nitrophenyl Ester Cleavage Due to Apolar Bonding. A Model for Biologically Significant Apolar Interactions[1,2]

Sir:

There has been much speculation concerning the nature and significance of apolar bonding in biologically active molecules, specifically in the maintenance of structure and mode of action of enzymes.[3] The interdependence of all the weak forces involved in the maintenance of enzyme structure and function makes difficult the direct study of apolar bonding in such a complex system. An insight into the role played by apolar bonding in enzymatic catalysis may be gained without this difficulty by studying a model system. This model system should exhibit some of the important characteristics of enzyme-catalyzed reactions, characteristics dependent upon apolar interactions.

We wish to report such a model system exhibiting substantial catalytic effects which are the result of prior formation of a 1:1 catalyst–substrate complex held together by apolar bonding. Since the catalyst I contains an anionic detergent portion and the substrate II a cationic detergent portion, interaction to form the catalyst–substrate complex appears to be similar to the strong binding observed between oppositely charged detergent molecules.[4] The demonstration of Michaelis-Menten (saturation) kinetics, product inhibition, large salt effects, and urea denaturation in this system serves to verify its enzyme-like nature.



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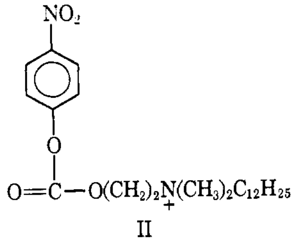

II

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(1) Part I in a series on selective catalysis.

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