

THE NOVEL DIMERISATION OF RADICAL ANIONS GENERATED ELECTROCHEMICALLY IN AQUEOUS
SOLUTION FROM MALEIMIDE

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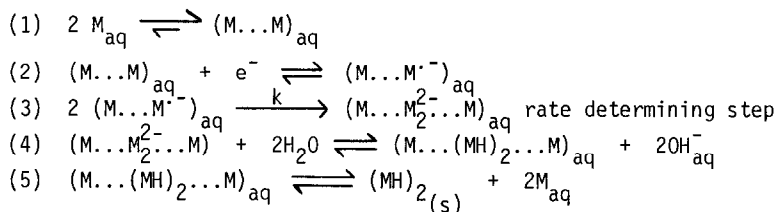
The one-electron reduction of maleimide yields the novel compound 1,2,3,4-butane-tetracarboxylic 1,2:3,4 diimide exclusively. Substrate-substrate hydrogen bonding was found to have a profound influence upon the pathways and kinetics of this unusual reaction.

Conjugated imides undergo facile electrochemical reduction in aqueous solutions. The kinetics and pH dependence of these reactions are consistent with electron transfer to an activated carbonyl group(1,2), but the overall course of the reactions may be atypical of electrochemical reduction of simple or conjugated carbonyl compounds. Reduction in acidic solution exemplifies this unique behaviour. Under these conditions, protonated carbonyl groups are usually reduced in a single two-electron process to the corresponding alcohols(1-3). The reduction of phthalimide is consistent with this, yielding the stable hydroxyphthalimidine(4). The reduction of maleimide yields only succinimide(5), despite the fact that the hydroxy compound is well known and is stable in aqueous solution(6).

The one-electron reduction of carbonyl compounds gives glycol dimers coupled at the reduced carbons, in high yields and with very few exceptions(1-3). These "hydrodimerisation" reactions are of considerable theoretical and practical importance because they involve facile and selective carbon-carbon bond formation under very mild conditions, in aqueous media. Preliminary studies(4,5,7) indicated that it was possible to transfer a single electron to the neutral imides, between pH 7-10, thereby forming the corresponding radical anions. The lifetimes of these species were seen to be extremely short in aqueous solution and it was postulated that they coupled to form dimeric products at diffusion-limited rates(4,5,7). It was speculated(4,7) that glycol dimers would be the products of the one-electron reduction of phthalimide, but this was found not to be the case(8). The present communication summarises the results of an investigation into the one-electron reduction of maleimide. The electrochemical measurements were complemented by physical and spectroscopic product characterisation and by yield determinations.

Different reaction pathways were found for low ($\leq 10^{-4}M$) and high maleimide concentrations ($> 10^{-4}M$). This value was obtained by monitoring the concentration dependence of the charge transfer process. Through use of the Ilkovic equation, the equilibrium constant was determined to be $pK = -3.9$ for the reaction $2M_{aq} \rightleftharpoons (M..M)_{aq}$. In addition, by use of the rotating disc electrode technique, measurements of the net diffusion coefficients of the reactant species as a function of reactant concentration gave a pK value of -4.0 . Therefore at formal concentrations above $\sim 10^{-4}M$ maleimide was found to exist in solution as an associated dimer $(M..M)_{aq}$ whose structure is probably analogous to that of the hydrogen-bonded entities in crystalline succinimide(9).

At high maleimide concentrations ($>10^{-4}\text{M}$) the kinetics of the reduction reaction were consistent with the following mechanism:



The electrochemical-chemical sequence of steps 2 and 3 were indicated by (10) the unusual Tafel slope of 40 mV per decade change in current, a reaction order of 3/2, pH independence of the current-voltage curve and the absence of significant reactant or product adsorption at the electrode surface. Although it was possible to identify the rate determining step as equation 3 this reaction was instantaneous on the fastest timescale of electrochemical investigation, $\sim 10^{-6}\text{s}$. Although equation 3 indicates that the chemical reaction is bimolecular, fractional reaction orders are often encountered in heterogeneous reactions,

The compatibility of a bimolecular reaction with an electrode kinetic reaction order of 3/2 may be shown as follows:

$$(6) \quad \text{rate} = 2 \frac{d(M\dots M^{\cdot-})}{dt} = 2k (M\dots M^{\cdot-})^2 = D \left[\frac{d^2(M\dots M^{\cdot-})}{dx^2} \right]_{x=0}$$

$$(7) \quad \therefore \left[\frac{d^2(M\dots M^{\cdot-})}{dx^2} \right]_{x=0} = 2(k/D) (M\dots M^{\cdot-})^2 \quad \text{where } D \text{ is the diffusion coefficient of the intermediate species.}$$

A solution of equation 7 is:

$$(8) \quad \left[\frac{d(M\dots M^{\cdot-})}{dx} \right]_{x=0} = (4kD/3)^{1/2} (M\dots M^{\cdot-})^{3/2}$$

The flux of the intermediate through the reaction layer in the steady state is:

$$(9) \quad J = -D \left[\frac{d(M\dots M^{\cdot-})}{dx} \right]_{x=0} = \frac{i}{zF} \quad \text{where } i \text{ is the current which flows in order}$$

to maintain the steady state concentration of $(M\dots M^{\cdot-})$ at the electrode-solution interface (i.e. $x=0$), therefore:

$$(10) \quad -i = zF (4kD/3)^{1/2} (M\dots M^{\cdot-})^{3/2}$$

At low overpotentials, $(E-E^0)$, then:

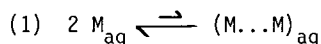
$$(11) \quad -i = zF (4kD/3)^{1/2} (M\dots M^{\cdot-})^{3/2} \exp 3zF(E-E^0)/2RT$$

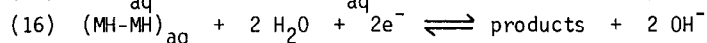
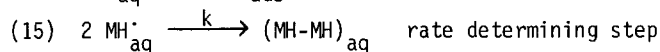
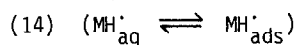
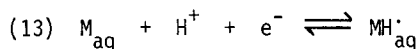
Under experimental conditions where equation 1 is biased to the right then $(M\dots M) \approx c_M/2$ where c_M is the formal concentration of maleimide and since $z=1$ we obtain:

$$(12) \quad -i = F(kD/6)^{1/2} c_M^{3/2} \exp 3F(E-E^0)/2RT$$

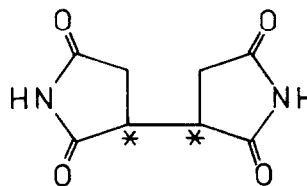
which predicts a reaction order in maleimide of 3/2 and a Tafel slope of $d(\log i)/dE$ of $(40 \text{ mV})^{-1}$ as observed experimentally.

And at formal concentrations below $\sim 10^{-4}$ the following mechanism is postulated to operate:





Under these conditions the reaction was dependent upon pH (reaction order in protons was 3/2), some intermediate adsorption at the electrode was evident, irreversible free radical dimerisation was indicated and the product of that dimerisation was unstable towards further reduction; electron transfer after the rate-determining step resulted in a net acceptance of two electrons per maleimide molecule. Hence, the entire reaction pathway was found to be a function of the reactant concentration because of the different properties of the reaction intermediates formed. Although this phenomenon is of considerable academic interest it will not be explored further in this preliminary communication because the reaction at high concentrations is most applicable to synthesis. A straightforward preparative electrolysis of maleimide(11) gives the following unconventional product in near 100% chemical yield. Gravimetric microanalysis of the product (d280-5) gave (calc./anal.): C(48.98%/48.94%), H(4.11%/4.07%), N(14.28%/14.22%), O by difference, and the molecular weight of 196 was confirmed by mass. spec. Only one product could be detected using HPLC (i.e. <<1% byproducts). A complete listing and analysis of the physical and spectroscopic properties (IR, ^1H NMR, ^{13}C NMR, MS, HPLC) of the product will be presented elsewhere(12).



(dl-meso) 1,2,3,4-butane-tetracarboxylic
1,2:3,4 diimide

In summary, complete specificity of unconventional reaction pathways may be achieved by carrying out the one-electron reduction of the conjugated maleimide in buffered aqueous solutions.

Acknowledgments

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- (11) Preparative electrolyses may be carried out under the following conditions: reference electrode - saturated calomel; working electrode - mercury pool; auxillary electrode - platinum, separated from working compartment by a medium porosity glass sinter; base electrolyte - concentrated buffer, pH 7.0 - 7.5 (13.6 g KH_2PO_4 + 2.6 g NaOH in 100 ml. distilled water). Procedure: Deoxygenate working electrode compartment by bubbling nitrogen through solution before and during electrolysis. Add 2 g finely ground, recrystallized starting material to form a suspension in a saturated solution. There should be continuous, rapid stirring during the electrolysis. Electrolyse at -850 ± 10 mV until the current decreases to $< 1\%$ of the initial steady state value. Filter the solid products from the chilled base electrolyte. Wash with several portions (10 ml) cold distilled water to remove salts. Chemical yields $> 95\%$, relative yield of recovered products $\gg 99\%$.
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