

## Electrode Mechanism Analysis Using the Reaction Order Approach. Application to Complex and Competing Mechanisms

VERNON D. PARKER

Laboratory for Organic Chemistry, Norwegian Institute of Technology, University of Trondheim, N-7034 Trondheim-NTH, Norway

For the electrode reaction,  $A \pm e^- \rightleftharpoons B$ , followed by homogeneous reactions of B the reaction orders  $R_{A/B}$  and  $R_X$  are given by (i) and (ii).

$$R_{A/B} = 1 + d \log V_c / d \log C_A \quad (i)$$

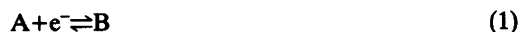
$$R_X = d \log V_c / d \log C_X \quad (ii)$$

In (i)  $R_{A/B}$  is the sum of the reaction orders in A ( $R_A$ ) and in B ( $R_B$ ) while in (ii)  $R_X$  is the reaction order in an additional reactant, X. For simple mechanisms the second terms in (i) and (ii) are constants and integers. Complex and competing mechanisms generally have two limiting cases at the concentration extremes where the second terms in (i) and (ii) are integers but at intermediate concentrations these terms are not constant and either increase or decrease with increasing  $\log C_A$  depending upon the values at limiting concentrations. This curvature along with the observed  $R_{A/B}$  are mechanistic criteria which can be used to derive rate laws for the complex and competing mechanisms. Rate constants are conveniently evaluated from  $(V_c)_{\text{relative}}$  vs.  $(C_A)_{\text{relative}}$  data obtained by simple arithmetical procedures and the corresponding data for the limiting cases. It was shown by comparison with data from digital simulation that the errors introduced by the approach are insignificant in comparison to experimental errors.

The rate laws for homogeneous reactions of electrode generated intermediates can be deduced directly from experimental data without assuming any theoretical models and carrying out the associated numerical calculations.<sup>1</sup> The primary experimental quantity in this "reaction order approach" is  $V_c$  which is defined as the value of

the experimental variable ( $V$ ) necessary to hold the experimental observable ( $O$ ) at a constant value ( $c$ ). For derivative cyclic voltammetry (DCV)<sup>2</sup>  $v$ , the voltage sweep rate, is the variable and  $R_f$ , the ratio of the derivative peaks on the backward and forward scans, is the observable. The other commonly used technique, double potential step chronoamperometry (DPSC)<sup>3</sup> has the pulse width  $\tau$  as the variable and the current ratio  $R_f$  as the observable.

For homogeneous reactions of B generated in electrode reaction (1) from substrate A, the quantity of mechanistic



significance is the reaction order  $R_{A/B}$  defined as the sum of the reaction orders in A ( $R_A$ ) and in B ( $R_B$ ) as in (2). The

$$R_{A/B} = R_A + R_B \quad (2)$$

reaction orders  $R_A$  and  $R_B$  are not directly separable using DCV and DPSC which necessitates the use of relationship (2). The inseparability of  $R_A$  and  $R_B$  by the electrochemical techniques can be a disadvantage in mechanism analysis but it is usually possible to distinguish between the various possibilities by other considerations.

In a previous work,<sup>1</sup>  $R_{A/B}$  was obtained from experimental data using relationship (3) in which  $z$  is the exponent of  $C_A$  in (4) necessary for that relationship to hold. For simple electrode mechanisms eqn. (4) does hold and  $R_{A/B}$  is an integer. Complex and competing mechanisms

characteristically give rise to apparent reaction orders which are concentration dependent. With these mechanisms relationship (4) does not hold and  $R_{A/B}$  can only be defined for narrow ranges of  $C_A$ . In these cases, the apparent rate law can be deduced for the particular ranges of  $C_A$ .

$$R_{A/B}=1+z \quad (3)$$

$$V_c/C_A^z=\text{constant} \quad (4)$$

The use of the "reaction order approach" as described above has been sharply criticized in some recent papers<sup>4,5</sup> and it has been stated that the approach is only applicable to simple reaction schemes where the rate is determined by a single step. These criticisms *are not valid* and result from a profound misunderstanding of what is meant by the method and how it is to be used. The purpose of this paper is to extend the "reaction order approach" using an alternative formulation to eqn. (4), to correct the misconceptions<sup>4,5</sup> which have been published regarding the method, and to show how it can be used in a quantitative manner for the derivation of the rate laws for complex and competing mechanisms of electrode generated intermediates.

## RESULTS AND DISCUSSION

The principles of the "reaction order approach" will first be outlined using simple electrode mechanisms as examples. The method will then be further developed in a qualitative way for complex and competing reaction mechanisms. Finally, the quantitative aspects of the method will be derived for a competing mechanism and the quantitative evaluation of

rate constants for both competing and complex mechanisms will be discussed.

*Simple reaction mechanisms.* These are regarded as reaction mechanisms with a single rate determining step. For these mechanisms theoretical calculations can readily be implemented to establish linear relationships of the form of eqn. (5).<sup>6</sup>

$$V_c=(\text{constant})kC_A^z \quad (5)$$

In eqn. (5)  $k$  is the rate constant for the process and  $z$  has the same meaning as in eqn. (3). First taking logarithms and then differentiating with respect to  $C_A$  results in eqn. (6) which

$$d \log V_c/d \log C_A=z \quad (6)$$

suggests a much more convenient method of analysis than employed when using eqn. (4). As implied by eqn. (6), a plot of  $\log V_c$  vs.  $\log C_A$  is linear with slope equal to  $z$ .

Thus, the "reaction order approach" described in the remainder of this paper involves the analysis of plots or correlations of  $\log V_c$  vs.  $\log C_A$  (or  $C_X$  where  $X$  is an additional reactant) in order to acquire data to formulate rate laws using  $R_{A/B}$ , obtained using relationships (6) and (3), and  $R_X$  obtained by the use of eqn. (7). The equation for the reaction order in  $X$ , *i.e.*  $R_X$ , is derived in the same manner as was (6).

$$R_X=d \log V_c/d \log C_X \quad (7)$$

Relationships between  $V_c$ , rate constants and substrate concentrations for both DCV and DPSC analysis of a number of simple electrode reaction mechanisms are summarized in Table 1. The values of  $z$  listed are observed to be equal to

Table 1. Theoretical rate constant and reaction order data for simple electrode mechanisms.

Mechanism <sup>a</sup>	$k(\text{DCV})$	$\frac{d \log v_{1/2}}{d \log C_A}$	$k(\text{DPSC})$	$\frac{d \log \tau_{1/2}}{d \log C_A}$
EC	$0.0781(F/RT)v_{1/2}$	0	$0.405/\tau_{1/2}$	0
ECE <sub>n</sub>	$0.1107(F/RT)v_{1/2}$	0	$0.272/\tau_{1/2}$	0
EC(dim)	$0.1173(F/RT)v_{1/2}/C_A$	1	$0.830/\tau_{1/2}C_A$	-1
Rad-Sub(2)	$0.151(F/RT)v_{1/2}/C_A$	1	$0.678/\tau_{1/2}C_A$	-1
Rad-Sub(3)	$0.444(F/RT)v_{1/2}/C_A^2$	2		-2

<sup>a</sup> For definitions of the mechanisms see Ref. 6.

0, 1 and 2 for first, second and third order mechanisms, respectively.

*Complex mechanisms with rate laws in which concentrations ( $C_A$  and  $C_B$ ) and the rate and equilibrium constants are separable.* These mechanisms are characterized by the rates being controlled by more than a single step but  $R_{A/B}$  is still independent of  $C_A$ . Reactions (8) and (9) with associated rate law (10) provide an example of this classification. If  $C_X$  is large (compared to  $C_B$ ) a



$$\text{Rate} = (k_8 k_9 / (k_{-8} + k_9 C_X)) C_B C_X \quad (10)$$

*Scheme 1. Mechanism 1.*

correlation of  $\log V_c$  vs.  $\log C_A$  will be linear with a slope equal to zero. Under the conditions described above, theoretical calculations are not capable of distinguishing between this mechanism and a simple first order reaction of B. However, the distinction can be made by varying  $C_X$  in the realm of values where  $k_{-8}$  and  $k_9 C_X$  are of comparable magnitude. This is most conveniently done using the "reaction order approach" and eqn. (7).

Other mechanistic schemes of this classification can result in fractional values of  $R_{A/B}$ . In such cases the correlation of  $\log V_c$  vs.  $\log C_A$  is linear with a fractional slope.

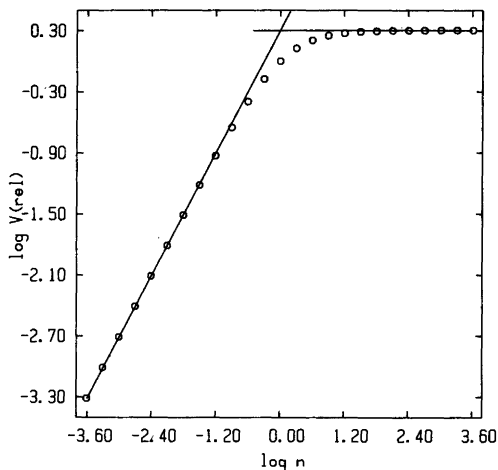
*Complex mechanisms with changing rate determining steps.* The characteristic feature of the kinetics of these reactions is that  $R_{A/B}$  of the limiting cases at extremes of  $C_A$  differ by 1. Mechanism 2 gives rise to this situation with  $R_{A/B}$  equal to 2 at low  $C_A$  and 1 at high  $C_A$ . This is obvious from the effect



$$\text{Rate} = (k_{11} k_{12} / (k_{-11} + k_{12} C_B)) C_B^2 \quad (13)$$

*Scheme 2. Mechanism 2.*

Acta Chem. Scand. B 38 (1984) No. 2



*Fig. 1. A plot of  $\log V_{rel}$  vs.  $\log n$  for mechanism 2.*

of  $C_A$  on the relative magnitudes of the two terms in the denominator of rate law (13). The "reaction order approach" analysis of this mechanism is illustrated graphically in Fig. 1. The intersecting straight lines of slopes 1 and 0 are for the two limiting cases. The curved line near the intersection is that predicted by rate law (13) when  $k_{-11}$  and  $k_{12} C_B$  are of comparable magnitude. The mechanistic criterion for this mechanism is that the  $\log V_c$  vs.  $\log C_A$  plot is curved downward. The construction of these curves is discussed later.

Another example of this type of behaviour, this time with  $R_{A/B}$  varying from 3 to 2 with increasing  $C_A$  is illustrated by mechanism 3. The  $\log V_c$  vs.  $\log C_A$  plot is curved downward in



$$\text{rate} = (k_{14} k_{15} / (k_{-14} + k_{15} C_B)) C_B^2 C_A \quad (16)$$

*Scheme 3. Mechanism 3.*

this case as well with the slopes for the limiting cases being 2 (at low  $C_A$ ) and 1 (at high  $C_A$ ). This mechanism is discussed in more detail later with the analysis of a practical example.

*Competing mechanisms with changing rate determining steps.* If two competing mechanisms are of the same reaction orders as is the case for the competing unimolecular reactions of B in mechanism 4, the existence of the competition cannot be detected by the "reaction order approach" or by the comparison with theoretical calculations. Such cases are rare since one



$$\text{rate} = (k_{17} + k_{18})C_B \quad (19)$$

#### Scheme 4. Mechanism 4.

or the other of competing reactions usually involves an additional reactant, X. When the latter is the case the competition is readily shown by the "reaction order approach" using eqn. (7).

Competing mechanisms of differing  $R_{A/B}$  characteristically change rate determining steps with changing  $C_A$ . An example of this is provided by mechanism 5 which involves competing first and second order reactions of B. The two limiting cases correspond



$$\text{Rate} = (k_{20} + k_{21}C_B)C_B \quad (22)$$

#### Scheme 5. Mechanism 5.

to  $k_{20} \gg \gg k_{21}C_B$  and  $k_{20} \ll \ll k_{21}C_B$ . the "reaction order approach" treatment of this case is illustrated in Fig. 2. At low  $C_A$ ,  $R_{A/B}$  is 1 and  $d \log V_c / d \log C_A$  is zero while at high  $C_A$ ,  $R_{A/B}$  is 2 and the slope is 1. When  $k_{20} \sim k_{21}C_B$  the  $\log V_c$  vs.  $\log C_A$  plot is curved upward. The intersecting straight lines describe the limiting cases. The construction of Fig. 2 is discussed in a following section.

Mechanism 6 is a final example and involves competing mechanisms with  $R_{A/B}$  equal to 2 and 3. As is obvious from rate

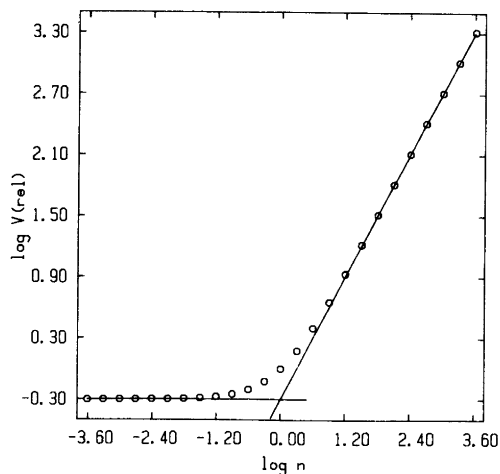


Fig. 2. A plot of  $\log V_{rel}$  vs.  $\log n$  for mechanism 5.



$$\text{Rate} = (k_{23} + k_{25}K_{24}C_A)C_B^2 \quad (26)$$

#### Scheme 6. Mechanism 6.

law (26), the two limiting cases are when  $k_{23} \gg \gg k_{25}K_{24}C_A$  and when  $k_{23} \ll \ll k_{25}K_{24}C_A$ . The plot of  $\log V_c$  vs.  $\log C_A$  for Mechanism 6 is curved upward in the region where  $k_{23} \sim k_{25}C_A$  with slopes of 1 and 2 for the limiting cases at low and high  $C_A$ , respectively.

*Derivation of the "reaction order approach" for competing mechanisms.* As an example we can take the competing first and second order reactions of B illustrated by mechanism 5 with rate law (22). There will be some concentration of A,  $C_A^0$ , where either experimental or theoretical data indicate that *on the average* for the time interval of the experiment,  $k_{20} = k_{21}C_B^0$ , where  $C_B^0$  is the average concentration of B. The concentration scale can then be expressed in multiples ( $n$ ) of  $C_A^0$ . If the reaction interval is sufficiently short,  $nC_B^0 \sim nC_A^0$  at all values of  $n$ . When this is the case, the rate law for mechanism (5) can be written as (27). In rate law

$$\text{Rate}=(1+n)n(k_{21}C_B^2) \quad (27)$$

(27) the only variable in the relative concentration  $n$  and the variations in the rate with concentration are a consequence of the changes in  $n(n+1)$ . There are three distinct cases for rate law (27) depending upon the magnitude of  $n$  and these are listed below.

Case 1.  
 $n \gg 1$ ,  $\text{Rate} = n^2 k_{21} C_B^2$        $R_B = 2.0$       (28)

Case 2.  
 $n \ll 1$ ,  $\text{Rate} = n k_{21} C_B^2$        $R_B = 1.0$       (29)

Case 3.  
 $n = 1$ ,  $\text{Rate} = n^{1.5} k_{21} C_B^2$        $R_B \sim 1.5$       (30)

There will be a rather wide concentration range on either side of  $n=1$  where fractional reaction

orders will be observed. The changes in  $V_c$  with  $n$  can readily be calculated by expressing  $C_A$  in units of  $n$  and assigning  $(V_c)_{\text{relative}}$  the value of 1 when  $n=1$ . Under these conditions,  $(V_c)_{\text{relative}}$  for mechanism 5 is given by eqn. (31).

$$(V_c)_{\text{relative}} = (n+1)/2 \quad (31)$$

Where the straight lines for the two limiting cases intersect is apparent by substituting very large and very small values of  $n$  in eqn. (31) which results in  $(V_c)_{\text{rel}}$  equal to  $n/2$  and  $1/2$ , respectively. That is,  $n$  equals 1 where the two lines intersect. There are also available, from theoretical calculations, linear equations for the two limiting cases. These equations can be expressed as (32) and (33) where  $c_{20}$  and  $c_{21}$  are constants and

$$(V_c)_{20} = c_{20} k_{20} \quad (32)$$

Table 2. Data for constructing reaction order curves for competing and complex electrode mechanisms.

$\log n$	$\log(V_{1/2})_{\text{relative}}$ $\log \frac{1}{2}(n+1)$ Mechanism 5	$\log \frac{1}{2}n(n+1)$ Mechanism 6	$\log 2n/(n+1)$ Mechanism 2	$\log 2n^2/(n+1)$ Mechanism 3
-3.612	-0.301	-3.914	-3.312	-6.924
-3.311	-0.301	-3.612	-3.011	-6.322
-3.010	-0.301	-3.311	-2.710	-5.720
-2.709	-0.301	-3.009	-2.409	-5.119
-2.408	-0.299	-2.708	-2.109	-4.517
-2.107	-0.298	-2.405	-1.810	-3.916
-1.806	-0.294	-2.101	-1.512	-3.318
-1.505	-0.288	-1.798	-1.217	-2.724
-1.204	-0.275	-1.479	-0.929	-2.134
-0.903	-0.250	-1.153	-0.653	-1.556
-0.602	-0.204	-0.806	-0.398	-1.000
-0.301	-0.125	-0.426	-0.176	-0.477
0	0	0	0	0
0.301	0.176	0.477	0.125	0.426
0.602	0.398	1.000	0.204	0.806
0.903	0.653	1.556	0.250	1.153
1.204	0.929	2.134	0.275	1.479
1.505	1.217	2.724	0.288	1.798
1.806	1.512	3.318	0.294	2.101
2.107	1.810	3.916	0.298	2.405
2.408	2.109	4.517	0.299	2.708
2.704	2.409	5.119	0.300	3.009
3.010	2.710	5.720	0.301	3.311
3.311	3.011	6.322	0.301	3.613
3.612	3.312	6.924	0.301	3.914

$$(V_c)_{21} = c_{21} k_{21} (nC_A^0) \quad (33)$$

can be used to evaluate the rate constants from  $V_c$  at the intersection.

In constructing  $\log(V_c)_{\text{rel}}$  vs.  $\log C_A$  curves using relationship (31) or comparable equations for the other mechanisms, it is convenient to vary  $n$  by factors of 2. This was done for mechanisms 2, 3, 5 and 6 and the data are summarized in Table 2. Eqn. (31) and comparable functions for the other mechanisms are listed as well.

The problem of determining rate and equilibrium constants from the  $(V_c)_{\text{rel}}$  vs.  $n$  data is reduced to the determination of the value of  $C_A^0$  in the experimental units. This is accomplished by finding the best fit of the experimental data to those in Table 2 for the particular mechanism in question. Once the value of  $C_A^0$  is established, the corresponding kinetic and equilibrium constants are readily evaluated using the linear equations for the two limiting case assuming very small and very large values of  $n$ .

*Comparison of theoretical data obtained by the "reaction order approach" and by digital simulation.* The equations for calculating the response are based on the analysis of initial rates for competing mechanisms. For competing mechanisms these equations can be expected to be exact at very low conversions of B. When conversion of B is significant,  $nC_B \sim nC_A^0$  no longer holds and some error is expected in  $(V_c)_{\text{rel}}$ . For the complex mechanisms the response equations are based on analogy to the competing mechanism. In this case it is difficult to make a prediction of

the possible error associated with the approach. In order to determine the range of applicability of the equations, digital simulation<sup>7</sup> was carried out to determine the DCV response to mechanisms 2, 3, 5 and 6. The data in Table 3 are a comparison of  $v_{0.500}$  values, *i.e.* the voltage sweep rates at which the derivative ratios are equal to 0.500, for mechanisms 3 and 6. This is equivalent to comparing the calculated rate constants. The data were obtained with  $n$  ranging from 0.0625 to 16. It is in this 256-fold concentration range that the curvature between the two limiting cases is evident. The correspondence is excellent. The maximum deviations (<2 %) were observed at the lowest  $n$  values for mechanism 6. Thus, the equations for both the competing (6) and complex (3) mechanisms accurately predict the response in these cases.

A quantitative comparison of the data obtained by the two methods can be made by determining  $(V_c)_{\text{rel}}$  at  $n=1$ . This will then give the error expected in rate constants evaluated by the "reaction order approach" assuming that the simulations are exact. Calculations were carried out for all four mechanisms over a range of conditions. For the competing mechanisms 6 and 5, data were obtained with  $V_c$  corresponding to  $v_{0.9000}$ ,  $v_{0.8000}$ ,  $v_{0.7000}$ ,  $v_{0.6000}$  and  $v_{0.5000}$ . The first two at low conversions are out of the range normally used in experimental studies but were included to test the theory that the error should disappear at low conversions. As expected, the errors were found to vary from about 0 at  $v_{0.9000}$  to about 1.7 % at  $v_{0.5000}$ . For the competing

Table 3. Comparison of data calculated by the "reaction order approach" and by digital simulation.<sup>a</sup>

$n$	Mechanism 3		Mechanism 6	
	$(V_c)_{\text{R.O.}}$	$(V_c)_{\text{sim}}$	$(V_c)_{\text{R.O.}}$	$(V_c)_{\text{sim}}$
16.0	30.2	30.1	136.0	134.4
8.0	14.3	14.2	36.0	35.8
4.0	6.45	6.41	10.0	10.0
2.0	2.67	2.67	2.99	2.99
1.0	1.00	1.00	1.00	1.00
0.5	0.333	0.334	0.374	0.374
0.25	0.100	0.100	0.156	0.155
0.125	0.0278	0.0279	0.0703	0.0695
0.0625	0.00735	0.00735	0.0332	0.0326

<sup>a</sup> The mechanisms are described in the text.  $V_c$  refers to the DCV sweep rate when the peak current ratio is equal to 0.500.

Table 4. Expected errors in the rate constants derived from the reaction order approach response equations.

Mechanism	c (in $V_c$ )	$(k_2/k_1)^a$	% Difference <sup>b</sup>
6	0.9000	3.657	0.00
6	0.8000	3.698	-0.50
6	0.7000	3.735	-0.64
6	0.6000	3.762	-1.30
6	0.5000	3.777	-1.69
5	0.9000	0.828	-0.11
5	0.8000	0.916	-0.35
5	0.7000	1.037	-0.71
5	0.6000	1.224	-0.95
5	0.5000	1.519	-1.74
3	0.7000	2.299	+1.78
3	0.6000	2.559	+0.81
3	0.5000	2.914	+0.23
2	0.7000	2.074	+1.39
2	0.6000	2.448	+0.72
2	0.5000	3.029	+0.05

<sup>a</sup> The appropriate rate constant ratio obtained from data for the limiting cases. <sup>b</sup> The difference in the rate constants calculated at  $n=1$  by the "reaction order approach" and by digital simulation.

mechanisms 3 and 2, the errors were observed to be very small at  $v_{0.5000}$  and increase to about 1.6 % at  $v_{0.7000}$ .

This comparison points out an interesting aspect of the equations. The response equations for the pairs, 6/3 and 5/2, are inverted with respect to each other in such a way that plots of the data are mirror images of each other. Likewise, the calculated expected errors in Table 4 show the same inverted relationship.

The conclusion that is warranted on the basis of the comparison of "reaction order approach" data with that obtained by digital simulation is that the errors introduced in using the former are quite small for the mechanisms which have been considered. Generally, there will be a 10 % or greater error in experimental data and the small errors expected from the inexactness of the "reaction order approach" data must be considered to be insignificant.

It is possible that larger errors may be associated with other mechanisms which have not been considered here. However, it is hardly conceivable that the errors will exceed those normally encountered in experimental work.

Theoretical data for mechanisms 3 and 6 have already been presented in graphical form.<sup>5</sup> In both cases, the correspondence between

$(V_1)_{\text{relative}}$  from the theoretical data and those calculated and given in Table 2 was found to be exact within the limits of error involved in taking the data from the published graph (Fig. 1 in Ref. 5).

An application of the "reaction order approach" data to an experimental case. Kinetic data obtained by DCV for the dimerization of 4-methoxybiphenyl cation radical in acetonitrile indicate that  $R_{A/B}$  goes from 3 at low values of  $C_A$  to 2 at higher values.<sup>8</sup> This kinetic behaviour was attributed to the competition between third and second order mechanisms, *i.e.* mechanism 6. The "reaction order approach" criterion for mechanism 6 is that the  $d \log (V_1)/d \log C_A$  plot in the intermediate range of  $C_A$  should curve upward with increasing  $C_A$ . The experimental  $d \log V_1/d \log C_A$  plot constructed from the data (Table 1 of Ref. 8) curves downward with increasing  $C_A$  reflecting the change in  $R_{A/B}$  from 3 to 2 as  $C_A$  increases. Thus, the mechanism proposed<sup>8</sup> is readily shown by the "reaction order approach" to be inconsistent with the experimental data. Furthermore, the "reaction order approach" requires that  $d \log V_1/d \log C_A$  have limiting values of 2 (at low  $C_A$ ) and 1 (at high  $C_A$ ) and increase as  $C_A$  increases at the intermediate concentrations. Of the mechanisms considered in

Table 5. A comparison of rate and equilibrium constants for the dimerization of 4-methoxybiphenyl cation radical assuming mechanism 3.

Quantity	"Reaction order approach" This work	Theoretical data Ref. 5
$k_{14}$	$4.14 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$	$4.07 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$
$k_{-14}$	$(2.98 \times 10^6 \text{ s}^{-1})^a$	
$k_{15}$	$(10^{10} \text{ M}^{-1} \text{ s}^{-1})^a$	
$K_{14}$	$(1.39 \times 10^{-2} \text{ M}^{-1})^a$	
$k_{15}K_{14}$	$1.39 \times 10^8 \text{ M}^{-2} \text{ s}^{-1}$	$1.65 \times 10^8 \text{ M}^{-2} \text{ s}^{-1}$

<sup>a</sup> Estimated values based on the assumption of diffusion control for reaction (15).

this paper, only mechanism 3 is consistent with the "reaction order approach" mechanism analysis. The inconsistency of the experimental data to the theoretical working curve for mechanism 6 and the compatibility with that for mechanism 3 has been pointed out.<sup>5</sup> A comparison of the rate constants obtained by the "reaction order approach" and by the use of theoretical working curves<sup>5</sup> along with the data from Ref. 8 is made in Table 5. The values of  $k_{14}$  and  $k_{15}K_{14}$  were obtained using the theoretical relationships for DCV for the limiting cases published some time ago.<sup>6</sup> The best fit of the experimental data to that in Table 2 for mechanism 3 was found to be when  $n=1/7$  at  $C_A$  equal to  $1.25 \times 10^{-4} \text{ M}$ , *i.e.* the lowest concentration used. This results in a value of  $8.75 \times 10^{-4} \text{ M}$  for  $C_A^\circ$ . The values of  $k_{14}$  and  $k_{15}K_{14}$  obtained by the "reaction order approach" and those values derived from the theoretical working curves<sup>5</sup> are identical within experimental error. The standard deviation of the experimental data from those in Table 2 was observed to be  $\pm 9.6\%$  when the mean value of  $100 ((V_i)_{\text{exp}} - (V_i)_{\text{calc}}) / (V_i)_{\text{calc}}$  was equal to  $-1.4$ . The best fit of the data was taken to be when the latter term was a minimum. Since the experimental data apparently has some scatter only integral fractions were used for  $n$  at the low concentration limit in the data fitting.

The additional details given in Table 5, *i.e.* the values of  $k_{-14}$ ,  $k_{15}$  and  $K_{14}$ , were obtained by assuming that reaction (15) is diffusion controlled with a rate constant equal to  $10^{10} \text{ M}^{-1} \text{ s}^{-1}$  which appears to be reasonable for the electron exchange reaction. This provides the estimate of  $K_{14}$ ,  $1.39 \times 10^{-2} \text{ M}^{-1}$ , which also appears to be reasonable since  $K_{14}$  must be small in order for rate law (16) to apply at all. Another useful

relationship to check for consistency is eqn. (34) which serves as an estimate of  $C_B^\circ$ . The value

$$C_B^\circ = k_{-14}/k_{15} = k_{14}/k_{15}K_{14} \quad (34)$$

obtained applying (34) is  $2.98 \times 10^{-4} \text{ M}$  which once again is reasonable since  $C_A^\circ$  was found to be equal to  $8.75 \times 10^{-4} \text{ M}$ .

## CONCLUSIONS

As emphasized earlier<sup>1</sup> the rate law for the reactions of an electrode generated intermediate can be deduced by the use of the "reaction order approach" directly from experimental data without resort to theoretical calculations. This work has clarified how the method can be used for both competing and complex mechanisms. In a mechanism study, the rate law usually is far more important than the evaluation of rate constants. The rate constants only have meaning after it is definitely established that the rate law corresponds to a particular reaction mechanism. There will usually be more than one mechanism that conforms to a particular rate law. Usually, a mechanism cannot be proven but can be described as the most likely on the basis of the fit of rate laws and other considerations involving the chemistry of the system in question. Once a mechanism assignment is deemed sufficiently credible, then any other additional detail such as rate and equilibrium constants should be evaluated. In terms of electrode mechanism analysis, this is when theoretical calculations are necessary, *i.e.* after the mechanism assignment. In this paper it was shown that when a rate law can be reduced to two limiting cases depending upon the



concentration of some species, A, B, or X, that it is only necessary to obtain theoretical data for the simple limiting cases and simple arithmetical procedures may be used to calculate the constants obtained from data in the intermediate concentration region.

The criticisms of the "reaction order approach" by Savéant and co-workers<sup>4,5</sup> are not valid and are very misleading. The "reaction order approach" is of most value for complex and competing mechanisms where the rate is determined by more than a single step.

In their attempt to discredit the "reaction order approach" in a sweeping manner, Savéant and co-workers<sup>5</sup> make the statement that they<sup>4</sup> have shown that we<sup>9</sup> have made an erroneous mechanism assignment for the dimerization of 9-substituted anthracene anion radicals. That statement<sup>5</sup> is misleading. What was shown<sup>4</sup> is that the kinetic data are consistent with a simple reversible dimerization. But this is not the point. The two mechanisms, simple dimerization and initial reversible complex formation between two anion radicals followed by reversible bond formation are kinetically indistinguishable.<sup>10</sup> The only differences in the rate laws for the two processes are the meaning of the constants multiplying the concentration terms. It was because of this that we were forced to search for other mechanistic criteria and based our assignment on that the apparent activation energies for the processes are very small.<sup>9</sup> The results of our initial study on these systems have been reinforced with further experiments and we have presented convincing arguments for our original mechanism assignment.<sup>10</sup>

The mechanism assigned by us<sup>8</sup> for the dimerization of 4-methoxybiphenyl cation radical is not consistent with the experimental data as shown in this study as well as in an earlier one.<sup>5</sup> However, this has nothing to do with the validity of the "reaction order approach" but shows that at the time that paper was submitted we were rather inept in its application. Obviously, this same mistake could not be made today using the "reaction order approach" in its present form.

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