Inverse Temperature Effects and Concentration Dependent Apparent First Order Rate Constants in Complex Ion Radical Reactions

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Ion radical reactions frequently consist of numerous coupled chemical and electron transfer equilibria prior to the rate determining step. Two consequences of this are (a) that the rates can show unusual temperature effects and (b) apparent first order rate constants can be concentration dependent. Both of these effects were found in two electrode reactions examined, the deprotonation of hexamethylbenzene cation radical in acetonitrile and the anodic asubstitution of bromine by trifluoroacetoxy during oxidation of 4-bromoanisole. In both cases inverse dependence of the reaction rates with temperature was observed and the apparent first order rate constants were dependent upon the substrate concentration. It is pointed out that these unusual temperature and concentration effects are powerful mechanism aids in the study of complex ion radical reactions. A method was developed for treating kinetic schemes in cases where concentration dependent apparent first order rate constants are observed.

A number of ion radical reactions have recently been shown to be more complex than previously believed, involving a number of chemical and electron transfer equilibria prior to the rate determining step.[1 – 5] A pertinent example is the pyridination of 9,10-diphenylanthracene[4,5] which had for many years been considered to be an established ECE_h* reaction involving rate determining reaction of the cation radical with pyridine.[6 – 8] The most recent work[4,5] has shown that it is necessary to include other equilibria in the rate law. The latter appears to be common situation, i.e. one or more

reversible steps take place before the final product forming reaction as illustrated by the simple case in eqns. (1) and (2). The observed rate constant for this reaction (k_{obs}) is then equal to $k_1 k_2/k_{-1}$; the reaction

$$(A^{\cdot})^{\pm} + B^{\mp} \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} A^{\cdot} - B \tag{1}$$

$$A^{\cdot} - B \overset{k_2}{\rightarrow} \text{products} \tag{2}$$

appears to be a simple second order process. The product of reaction (1) is usually highly reactive and present in low concentration and not detectable. If equilibrium (1) is favoured by low temperatures, as is expected for an association reaction and reaction (2) is enhanced at higher temperatures, an unusual effect of temperature on the overall reaction rate is to be expected.

Another very frequently encountered situation in reactions of ion radicals is that the rate law has a term due to the substrate in the denominator. Reactions which appear to be first order in ion radical can give apparent first order rate constants which are substrate concentration dependent.
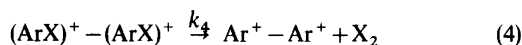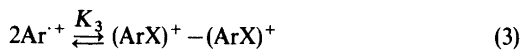
It is the purpose of this paper to demonstrate that the two complexities mentioned in the previous paragraphs, i.e. the unusual temperature dependence and concentration effects, can be used to advantage in mechanism studies and are convincing evidence of the complex nature of reaction[9] giving rise to the behaviour.

RESULTS AND DISCUSSION

Temperatures effects. Practically all simple one step reactions show an increase in rate with increas-

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* The subscript, h, indicates that the second electron transfer takes place in solution rather than at the electrode.

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ing temperature. Arrhenius plots for these simple cases are usually linear over a fairly wide temperature range.[9] Complex reactions can give Arrhenius plots which are curved either concave upward or concave downward depending upon the nature of the complexity. Another type behaviour has recently been noted for a complex ion radical reaction. The dehalodimerization of 4-halo-N,N-dimethylanilines produced Arrhenius plots which were not linear and very nearly flat, i.e. a fifty degree temperature change only brought about a rate change of about a factor of 2.[1] The unusual temperature effect was attributed to a reversible dimerization followed by loss of halogen, symbolized in eqns. (3) and (4). Thus, equilibrium (3), as suggested for (1), was proposed to be favored by lower temperatures which has the effect of cancelling the normal

$$2Ar^{\cdot+} \underset{}{\overset{K_3}{\rightleftarrows}} (ArX)^+ - (ArX)^+ \tag{3}$$

$$(ArX)^+ - (ArX)^+ \overset{k_4}{\rightarrow} Ar^+ - Ar^+ + X_2 \tag{4}$$

temperature dependence of the rate determining step (4). Even more extreme cases are to be expected where the effect on the equilibrium as in (1) or (3) is so great that the predominant temperature effect is associated with the equilibrium and the overall effect is an inverse one.

Complex rate laws and electrode response. As an example we can take the disproportionation mechanism (eqns. 5 and 6). Application of the steady

$$2A^{\cdot+} \underset{k_{-5}}{\overset{k_5}{\rightleftarrows}} A^{2+} + A \tag{5}$$

$$A^{2+} \overset{k_6}{\rightarrow} products \tag{6}$$

state approximation on A^{2+} provides rate law (7).

$$Rate = k_6 k_5 [A^{\cdot+}]^2/(k_6 + k_{-5}[A]) \tag{7}$$

Even in this relatively simple case, further assumptions have to be made in order to be able to write flux expressions for the various species to be used in numerical calculations of the theoretical response. Two limiting cases have been treated for linear sweep voltammetry (LSV).[10] The first is when $k_6 \gg k_{-5}[A]$ and results in rate law (8), i.e. the "fast equilibrium" case. The other limit is when $k_6 \gg k_{-5}$ [A] and this results in the rate determining electron transfer case (9). In between these two extremes

$$Rate = k_6 K_5 [A^{\cdot+}]^2/[A] \tag{8}$$

$$Rate = k_5 [A^{\cdot+}]^2 \tag{9}$$

where apparent first order rate constants (8) and second order rate constants (9) are observed, there must be a range where $k_6/k_{-5}[A]$ varies from about 0.01 to 100 under which circumstances the apparent reaction order is expected to vary in the range 1.0 to 2.0. Even when rate law (8) is assumed, it has recently been shown[11] in analogy to the treatment of a similar case[12] that reaction orders greater than unity are expected when K_5 is not far removed from 1.0.

The discussion in the preceding paragraph could lead to a pessimistic attitude regarding the value of carrying out kinetic studies by transient electrochemical techniques on reactions with mechanisms too complex to obtain theoretical response data. However, if one keeps in mind that the purpose of the kinetic investigation is to describe the mechanism as best one can, the evaluation of microscopic rate constants may not be essential. For example, (7) can be converted into usable form by dividing each term by [A] to give (10). We can then define "k_{obs}" as in (11) and write rate law (12). The concentration dependent rate "constant" "k_{obs}" can

$$rate = k_6 K_5 [A^{\cdot+}]^2 [A]^{-1}/((k_6/k_{-5})[A]^{-1} + 1) \tag{10}$$

$$\text{"}k_{obs}\text{"} = k_6 K_5/((k_6/k_{-5})[A]^{-1} + 1) \tag{11}$$

$$Rate = \text{"}k_{obs}\text{"}[A^{\cdot+}]^2 [A]^{-1} \tag{12}$$

then be used in an approximate way in conjunction with theoretical data calculated for rate law (8). The concentration dependence of "k_{obs}" gives an indication of the magnitude of the rate constant ratio, k_6/k_{-5}.

The procedure described in the previous paragraph for using electrode response data for complicated reaction mechanisms for which theoretical data are not available should make it possible to drawn mechanistic conclusions based on the kinetic data. Experimentally, data often fit the first order working curves for various techniques reasonably well. The observation that the apparent first order rate constants are concentration dependent should make one suspicious that the reason for the latter is that the rate law is similar to (7) and the working curve is not directly applicable.

Substitution of bromine by trifluoroacetoxy during oxidation of 4-bromoanisole in dichloromethane—trifluoroacetic acid. The derivative linear sweep voltammogram for the oxidation of 4-bromoanisole (BrAn) in dichloromethane—trifluoroacetic acid (DCM—TFA, 9/1) showed in addition to the derivative peak for the primary oxidation process, a peak about 200 mV more anodic due to the oxidation of a reaction product. The peak matched the primary oxidation peak during voltammetric oxidation of the suspected product, 4-trifluoroacetoxyanisole. Highly oxidizing solutions are formed upon exhaustive electrolysis and attempts to isolate the primary product have so far not met with success. However, during the time scale of cyclic voltammetry the process appears to be restricted to the formation of the cation radical which then reacts at a measureable rate to give a primary product which can be assigned the 4-trifluoroacetoxyanisole structure on the basis of the voltammetric peak matching. Further product studies are in progress.

Mechanism analysis. Mechanism analysis can be accomplished by use of eqn. (13) which has recently been presented for the dependence of the derivative peak current ratio on the voltage sweep rate during derivative cyclic voltammetric (DCV) ... kinetic studies.[13] The mechanistic conclusions can be made

$$\ln R_{\mathrm{I}}' = m \ln (1/v) + c' \qquad (13)$$

by comparing the slope m in the logarithmic correlation of the derivative peak current ratio R_{I}' with the inverse of the voltage sweep rate v to theoretical data calculated for the various electrode mechanisms. Table 1 gives a summary of m values and correlation

Table 1. Derivative cyclic voltammetric mechanism analysis of the oxidative substitution of bromine from 4-bromoanisole.

C/mM[b]	m[c]	c'[d]	r[e]
0.25	−0.347	−1.051	0.997
0.50	−0.363	−1.184	0.998
1.00	−0.407	−1.298	0.999
1.00	−0.360	−1.461	0.998
1.00	−0.368	−1.458	0.986

[a] Solvent = DCM − TFA (9/1), $\mathrm{Bu_4NBF_4} = 0.1$ M, $v = 1$, 2, 4, 7, and 10 V/s. Temperature = 21 °C, $E_{\mathrm{sw}} - E_{\mathrm{rev}} = 500$ mV. [b] Substrate concentration. [c] Slope. [d] Intercept. [e] Correlation coefficient for the correlation of data according to eqn. (13).

Table 2. Concentration dependence of observed rate constants during the oxidation of 4-bromoanisole in DCM − TFA.[a]

$v/\mathrm{V\ s^{-1}}$	$k_{\mathrm{obs}}/\mathrm{s^{-1}}$ at $C°/\mathrm{mM}$		
	0.25	0.50	1.00
1.00	5.72	8.39	11.9
2.00	7.09	9.29	10.9
4.00	6.26	8.59	9.94
7.00	7.68	10.0	10.3
10.0	6.82	8.43	9.88
	6.71(75)	8.94(69)	10.6(8)

[a] Measurements at 21 °C by derivative cyclic voltammetry. Supporting electrolyte was $\mathrm{Bu_4NBF_4}$ (0.1 M) and the solvent ratio was 9/1. Data treated according to procedures in Ref. 21.

coefficients for the sweep rate range 1 to 10 V s⁻¹. The value of the slope found, -0.369 ± 0.023, compares very closely with the theoretical value, -0.378, for the first order $\mathrm{ECE_h}$ mechanism under the conditions of the analysis. Thus, the data can be considered an excellent fit to the theoretical relationship and the mechanism could be assigned as $\mathrm{ECE_h}$ on this basis.

However, if one considers the rate data in Table 2, where the rate constants are calculated assuming the $\mathrm{ECE_h}$ mechanism, a different conclusion must be drawn. Although the rate constants at a particular concentration are consistent with the mechanism, the observed values are concentration dependent. The latter implies that the simple $\mathrm{ECE_h}$ does not describe the mechanism of the reaction.

The conclusion drawn in the previous paragraph is strongly reinforced by the effect of temperature on the apparent first order rate constant. The data in Table 3 show that the apparent first order rate constant is nearly temperature independent in the range from 21 to 2 degrees but actually increases significantly at lower temperature. This inverse temperature effect is surely indicative of a complex mechanism.
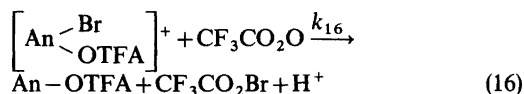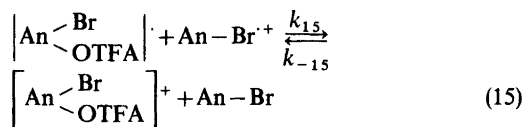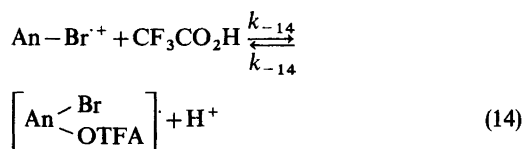
Kinetic analysis. Since the data at a particular substrate concentration fits the $\mathrm{ECE_h}$ theoretical relationships we can use the rate law for this mechanism as a basis and try to make appropriate modification to the mechanism to account for the concentration and temperature effects. The steps involved in the formation of 4-trifluoroacetoxyanisole from the cation radical can be summarized as in eqns. (14)

Table 3. Effect of temperature on the apparent first order rate constants for the oxidative dehalogenation of 4-bromoanisole.

$T/°C$	k/s^{-1}	Mean (S.D.)[a]
21	22.1	
21	22.3	
21	22.1	22.10(11)
21	22.0	
21	22.2	
12	20.4	
12	20.4	
12	20.4	20.40(4)
12	20.5	
12	20.4	
2	21.2	
2	21.2	
2	21.2	21.30(13)
2	21.5	
−10	37.6	
−10	37.3	
−10	36.7	36.6(10)
−10	36.1	
−10	35.1	

[a] All measurements made at a substrate concentration of 2.0 mM in DCM − TFA (9/1) containing Bu_4NBF_4 (0.1 M) at 10.0 V s^{-1}. Each rate constant is the result of 10 measurements treated according to procedures in Ref. 21.

to (16). In the ECE_h mechanism, k_{14} is the rate determining step, k_{-14} is neglected and k_{15} and k_{16} are considered to be large. The rate law under these conditions is given by (17). In order to bring in some second order behaviour into the mechanism and the rate law we can include the forward step (15)

$$An - Br^{\cdot +} + CF_3CO_2H \underset{k_{-14}}{\overset{k_{14}}{\rightleftharpoons}}$$

$$\left[An \overset{Br}{\underset{OTFA}{<}} \right]^{\cdot} + H^+ \tag{14}$$

$$\left| An \overset{Br}{\underset{OTFA}{<}} \right|^{\cdot} + An - Br^{\cdot +} \underset{k_{-15}}{\overset{k_{15}}{\rightleftharpoons}}$$

$$\left[An \overset{Br}{\underset{OTFA}{<}} \right]^+ + An - Br \tag{15}$$

$$\left[An \overset{Br}{\underset{OTFA}{<}} \right]^+ + CF_3CO_2O \overset{k_{16}}{\longrightarrow}$$
$$An - OTFA + CF_3CO_2Br + H^+ \tag{16}$$

$$Rate = k_{14}[An - Br^{\cdot +}] [CF_3CO_2H] \tag{17}$$

and take into account the reverse reaction (14). Application of the steady state approximation on the intermediate cyclohexadienyl radical then results in rate law (18). We can treat (18) similar to the way in which (10) was transformed to (12) by first dividing each term by $[An - Br^{\cdot +}]$ and then defining "k_{obs}" as in (19) which then results in rate law (20).
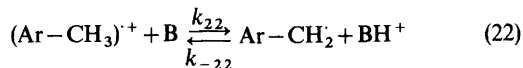
$$Rate = k_{14}k_{15}[An - Br^{\cdot +}]^2[CF_3CO_2H]/$$
$$(k_{-14}[H^+] + k_{15}[An - Br^{\cdot +}]) \tag{18}$$

$$"k_{obs}" = k_{14}k_{15}/(k_{-14}[H^+]$$
$$[An - Br^{\cdot +}]^{-1} + k_{15}) \tag{19}$$

$$Rate = "k_{obs}" [An - Br^{\cdot +}] [CF_3CO_2H] \tag{20}$$

Rate law (20) describes a mechanism which can account for both the temperature dependence and the concentration dependent apparent first order rate constants.* Equilibrium (14) is an example of the general case (1) and would be expected to be shifted to the right at low temperatures. Including the electron transfer in the rate expression brings into the reaction a second order element the importance of which is concentration dependent. The exact nature of the product forming reaction is open to question. The bromine could leave in alternative oxidation states, 0 or −1, although the latter seems unlikely. Settling this question is the objective of further studies.

Deprotonation of hexamethylbenzene cation radical in acetonitrile. The deprotonation of arenemethyl cation radicals has been studied in detail in aprotic[14−16] as well as in acidic solvents.[3] The most recent studies in acetonitrile[14−16] have resulted in somewhat conflicting views as to the form of the rate law describing the processes. Bewick and co-workers[14,15] treat the data as an ECE_h type of mechanism with the observed rate constant being equal to k_{22}. Schmid Baumberger[16] points out that the linear sweep voltammetry data in dry acetonitrile indicates a much more complex situation in which the observed rate constant must include contributions from steps (22), (23) and (24).
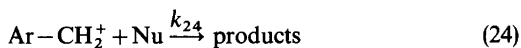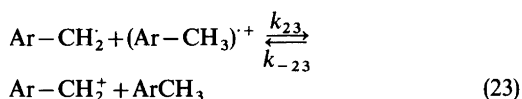
$$Ar - CH_3 - e \rightleftharpoons (Ar - CH_3)^{\cdot +} \tag{21}$$

$$(Ar - CH_3)^{\cdot +} + B \underset{k_{-22}}{\overset{k_{22}}{\rightleftharpoons}} Ar - CH_2^{\cdot} + BH^+ \tag{22}$$

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* The cation radical concentration is proportional to $[An - Br]_o$.

Table 4. Derivative cyclic voltammetric analysis of the deprotonation of hexamethylbenzene cation radical in acetonitrile.[a]

Substrate	C/mM^b	m^c	c^d	r^e
HMB	0.10	−0.284	−2.315	0.987
HMB	0.25	−0.330	−2.712	0.976
HMB	0.50	−0.289	−2.613	0.999
HMB(d_{18})	0.25	−0.260	−2.028	0.988
HMB(d_{18})	0.50	−0.264	−2.215	1.000
HMB(d_{18})	1.00	−0.266	−2.581	0.999
HMB(d_{18})	1.00	−0.238	−2.434	1.000

[a] In acetonitrile at 22 °C, Bu$_4$NBF$_4$ (0.1 M) at 100, 200, 300, and 400 V s^{-1}, $E_{sw} - E_{rev} = 500$ mV. [b] Substrate concentration. [c] Slope. [d] Intercept. [e] Correlation coefficient for the correlation of the data according to eqn. (13).

$$Ar-CH_2^{\cdot} + (Ar-CH_3)^{\cdot+} \underset{k_{-23}}{\overset{k_{23}}{\rightleftarrows}}$$

$$Ar-CH_2^+ + ArCH_3 \tag{23}$$

$$Ar-CH_2^+ + Nu \xrightarrow{k_{24}} products \tag{24}$$

Mechanism analysis. Derivative cyclic voltammetric analysis of the oxidation of both hexamethylbenzene (HMB) and HMB (d$_{18}$) was carried out according to eqn. (13). The correlation parameters are summarized in Table 4. The average value of m, -0.276 ± 0.029, fits the theoretical value for the disproportionation mechanism, -0.263 under the conditions of the measurements, quite closely. The expected slope for the ECE$_h$ mechanism, -0.378, lies far out of the range of experimental error and thus that mechanism is effectively excluded. The latter is not surprising in light of the LSV study[16] which resulted in dE^p/d log v equal to 19 mV/decade in close agreement with the theoretical value for a second order reaction.

Thus, mechanism analysis both by LSV[16] and by DCV are consistent with the disproportionation mechanism or any mechanism having a rate law of the form of (8). It would appear to be justifiable to accept the results from the two independent techniques and fit the rate law with the most reasonable alternative mechanism. However, the previous discussion of the reactions of 4-bromoanisole cation radical suggests that it is necessary to proceed with caution. Even though the process appears to fit the criteria for the simple form of rate law (8), tests for complexity must be carried out. As before, these tests are provided by variable concentration and temperature studies.

Table 5. The dependence of the apparent first order rate constant for deprotonation of hexamethylbenzene cation radicals on the substrate concentration.[a]

Substrate	C/mM^b	k_{obs}/s^{-1c}
HMB	0.10	172
HMB	0.25	372
HMB	0.50	585
HMB	1.00	1152
HMB(d_{18})	0.125	41.4
HMB(d_{18})	0.25	53.8
HMB(d_{18})	0.50	101
HMB(d_{18})	1.00	183

[a] Measured in acetonitrile at 22 °C, estimated water content 10 mM, supporting electrolyte was Me$_4$NBF$_4$ (sat., ~0.1 M). [b] Substrate concentration. [c] Measured by DCV according to Ref. 21 at 200 V s^{-1}, $E_{sw} - E_{rev} = 500$ mV and theoretical data for the rate law, rate = $k_{obs}[A^{\cdot+}]^2[A]^{-1}$.

The data in Table 5 show that the apparent first order rate constants for both HMB(d$_{18}$) cation radicals are *indeed* concentration dependent. This is clearly inconsistent with the simple rate law (8). The effect of temperature on the apparent first order rate constants is equally revealing. For both substrates, the apparent first order rate constants increase with decreasing temperature, a clear indication of an equilibrium favored by lower temperature prior to the product forming step (Table 6).

Kinetic analysis. Since the LSV and DCV mechanism analyses are both consistent with a rate law of the form of (8), we can use this as our basis for

Table 6. Kinetic data for the deprotonation of hexamethylbenzene cation radicals in acetonitrile as a function of the temperature.[a]

$T/°C$	k_{obs}(HMB)/ s^{-1b}	k_{obs}(HMB-d)/ s^{-1b}	k_H/k_D
30	427(12)	103(0)	4.2
22	664(2)	137(1)	4.8
12	877(38)	180(1)	4.9
2	816(12)	207(4)	4.0

[a] Freshly distilled acetonitrile, estimated water content 10 mM, Me$_4$NBF$_4$ (sat., ~0.1 M). [b] Rate constants measured by DCV according to Ref. 21 at 200 V s^{-1}, $E_{sw} - E_{rev} = 500$ mV using theoretical data for the rate law, rate = $k_{obs}[A^{\cdot+}]^2[A]^{-1}$. The numbers in parentheses refer to the standard deviation in 5 replicate measurements.

arriving at an expression for "k_{obs}" the concentration dependent apparent first order rate "constant".

Application of the steady state approximation on $ArCH_2^+$ (eqns. 22 – 24) results in rate law (25), and assuming that reaction (22) is in equilibrium, (26). Dividing each term in (26) by $[ArCH_3]$ and

$$Rate = k_{23}k_{24}[ArCH_2^.][ArCH_3^{.+}][Nu]/ (k_{24}[Nu]+k_{-23}[ArCH_3]) \qquad (25)$$

$$Rate = k_{24}K_{23}[ArCH_3^{.+}]^2([B]/[BH^+])[Nu]/ ((k_{24}/k_{-23}[Nu]+[ArCH_3]) \qquad (26)$$

defining "k_{obs}" as in (27) results in rate law (28). The rate law, or more precisely, the form of "k_{obs}"

$$"k_{obs}" = k_{24}K_{22}K_{23}([B]/[BH^+])[Nu]/ ((k_{24}/k_{-23})[Nu][ArCH_3]^{-1}+1) \qquad (27)$$

$$Rate = "k_{obs}"[ArCH_3^{.+}]^2[ArCH_3]^{-1} \qquad (28)$$

accounts for the concentration dependence of the apparent first order rate constants. The inverse temperature effect must be accounted for by equilibrium (22) or (23). It does not appear likely that (23) would be affected significantly by temperature. The temperature should affect the two redox couples in the same way and since they are in opposite directions, the overall effect should be small. The latter suggests that the inverse temperature effect is associated with equilibrium (22). A reasonable interpretation is that BH^+, which could be the conjugate acid of either acetonitrile or water, is more highly solvated than the delocalized cation radical which could give rise to a significant thermal effect. An analogy can be drawn from the disproportionation of tetraphenylethylene anion radicals (eqn. 29),[18] written in the reverse direction for direct comparison. The equilibrium constant, K_{-disp}, increases with decreasing temperature and this is attributed to

$$TPE^{2-}, 2Na^+ + TPE \xrightleftharpoons{K_{-disp}} 2TPE^{.-} + 2Na^+ 2Na^+(solv) \qquad (29)$$
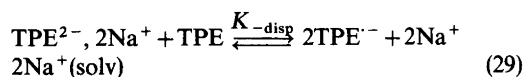
the increasing difficulty in desolvating the alkali metal counter ions in the reverse direction as the temperature increases. This interpretation is speculative and further work is required for a more definitive explanation.

It is not the objective of this paper to discuss the mechanism of arenemethyl cation radical de-

protonation in detail. The deuterium kinetic isotope and the sensitivity of the rate of the reaction to the water concentration certainly have mechanistic consequences. For the present it suffices to say that the value of k_H/k_D is of the order of 4 but depends on the water concentration. Data from Tables 5 and 6 may appear to be somewhat inconsistent and this is due to the latter. The two sets of experiments were conducted using different stock solutions of solvent-supporting electrolyte and presumably had different water concentration. If water is nearly completely excluded by conducting the the experiments over neutral alumina,[19] product adsorption on the electrode becomes rather severe and reverse current for the reduction of the cation radical is not observed which indicates that the rate is much higher under anhydrous conditions. A thorough investigation including structural effects is underway.

Conclusions. The data and discussion presented here serve to demonstrate the general complexity of ion radical reactions. It has been customary in the past to discuss these reactions in terms of simple elementary processes. For example, the deprotonation of arenemethyl cation radicals is one of the most actively studied organic electrode processes and is, with the exception of our recent papers,[3,16], invariably discussed in terms of the simple cleavage of the carbon hydrogen bond followed by fast irreversible steps. It is becoming increasingly apparent that very few ion radicals reactions are so simple as to be amenable to such treatment.

It is also apparent that theoretical calculations for the usual type simple mechanisms, EC, ECE$_h$, *etc.*, are based on models less complex than the majority of the ion radical reactions. The objective of this paper has been to show that the complexity of the reactions does not leave the situation hopeless in terms of gaining a mechanistic understanding of the reactions. The concentration and temperature effects as applied in this paper provide powerful mechanistic probes capable of immediately showing the complex nature of the reactions. The approximate treatment based upon "k_{obs}," the concentration dependent apparent first order rate "constant" allows mechanism analysis to be carried out even in very complex cases which are not amenable to definitive theoretical analysis. In this respect, it should be pointed out that homogeneous kinetic techniques, in which some observable such as the absorbance of a reactant is monitored, could give very little kinetic and mechanism detail in such

cases. One might wonder why the apparent first order rate constants are observed in the first place when the effective rate constant is changing with changes in the substrate concentration. The answer to this question must lie in the fact that although the concentration gradient of substrate is quite steep very close to the electrode, it is not nearly so in the region of the diffusion layer where most of the reaction takes place and the effective change in substrate concentration is obscure during a single experiment.

EXPERIMENTAL

The apparatus and procedures used were essentially the same as those reported in recent papers from this laboratory.[4,20,21]

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