

Short Communications

Simple and Exact Determination of Apparent Activation Energies of Electrode Processes

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Rate constants for homogeneous chemical reactions coupled to charge transfer at electrodes can be obtained by comparison of the response to a perturbation to theoretical working curves calculated for the particular transient technique.¹ In order to use the theoretical data for rate constant determination, it is necessary to know the mechanism of the reaction being studied. If the mechanism is unknown or the experimental data cannot be correlated with those for any known mechanisms or the kinetic diffusion problem relating to the particular mechanism has not been solved, very little information can be obtained from the electrode response data. It is the purpose of this note to point out that it is possible to obtain the apparent activation energy for an electrode process even in situations as described above where the rate constant cannot be determined.

Theoretical working curves for electrode response consist of plots of some observable as a function of the rate constant and an experimental variable [eqn. (1)]. At a particular value of the observable

$$\text{Observable} = f(k \cdot \text{Variable}) \quad (1)$$

and from the known value of the experimental variable, the rate constant can be obtained simply from the working curve. For example, two very common techniques, cyclic voltammetry and double potential step chronoamperometry, have working curves based on relationships (2) and (3), respectively. In (2) I_b^0/I_f^0 is the ratio of the backward to

$$I_b^0/I_f^0 = f(k/v) \quad (2)$$

$$I_b/I_f = f(k\tau) \quad (3)$$

forward peak currents and v is the voltage sweep rate. In (3) I_b/I_f is the ratio of the currents at 2τ and at τ , where τ is the pulse width. Relationships (1) to (3) are written for first order reactions, for the second order case there is a concentration term on the right-hand side of each equation. The fundamental variables for the two techniques are the voltage sweep rate and the pulse width, respectively.

The method by which the activation energies are obtained is very simple. The current ratio in either (2) or (3) can be adjusted to a convenient value for measurement at a particular temperature by adjusting the appropriate variable v or τ . When the temperature is changed the experimental variable (v or τ) can be fine-tuned so that the current ratio remains unchanged. Thus, the relative magnitudes of the variables at the two temperatures are related to the relative values of the rate constants. Carrying out the analysis over a range of temperatures then provides a precise measure of the Arrhenius activation energy for the process.

The first order cleavage reaction of 9-chloroanthracene anion radical was chosen to demonstrate the method by derivative cyclic voltammetry.² The mechanism of this reaction is generally accepted to be of the EC type [eqns. (4) and (5)].³ The activation energy for the process in DMF has been

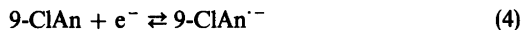


Table 1. Arrhenius activation energy determination for the cleavage of 9-chloroanthracene anion radical in *N,N*-dimethylformamide.^a

$T/^\circ\text{C}$	$v/\text{V s}^{-1}$	R_i
34.5	101	0.469 (± 0.006)
23.0	50.0	0.470 (± 0.025)
15.0	23.2	0.469 (± 0.009)
-5.0	2.74	0.461 (± 0.011)

^a Supporting electrolyte, Bu_4NBF_4 (0.1 M). Correlation of the data according to eqn. (6) gave a correlation coefficient of 0.996.

reported to be equal to 15.2 kcal/mol with k_5 equal to 116 s^{-1} at 25°C .⁴ At 50 V s^{-1} the derivative peak current ratio (R'_i) was found to be equal to 0.470 at 23°C . A summary of data for four temperatures at which the sweep rate was adjusted to give the desired value of R'_i is given in Table 1. The R'_i values are the mean of ten determinations after fine-tuning of the sweep rate. In order to calculate the Arrhenius activation energy the data was treated according to eqn. (6) in accordance with the previous discussion. The value found, 15.2 kcal/mol is nearly the same as that observed using

$$\ln i = (-E_a/R)(1/T) + c \quad (6)$$

rate constants determined by derivative cyclic voltammetry.⁴ The data surely demonstrate the utility of the method.

It is important to emphasize that the method reported here for the activation energy determination does not rely on any assumptions regarding the mechanism of the electrode process. There is no need to resort to the use of a working curve and the activation energy is obtained directly from the experimental parameters. The method should prove to be of great value in mechanism determination of electrode processes.

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Received October 17, 1980.