

## A SINGLE SWEEP CYCLIC VOLTAMMETRIC METHOD FOR DETERMINING THE RATE OF DECOMPOSITION OF IONIC SPECIES GENERATED ON A STATIONARY ELECTRODE AND UNDERGOING ECE MECHANISM

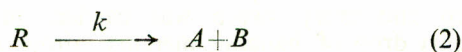
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**Abstract.** The method for the evaluation of rate of decomposition of ionic species in the following sequence of reactions  $O + e \rightleftharpoons R$ ,  $R \xrightarrow{k} A + B$  (product),  $2A \rightarrow A_2$ ,  $A_2 + ne \rightarrow A_2^{ne}$  is described and applied to the decomposition of 4-nitrobenzyl chloride anion radical. The value  $75(\pm 25) \text{ sec}^{-1}$  thus obtained for  $k$  for 4-nitrobenzyl chloride anion is believed to be more accurate than the value  $10 \text{ sec}^{-1}$  reported earlier.

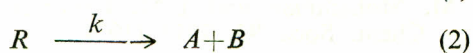
Many ionic species generated from parent molecules by electro reduction or oxidation are unstable. These species undergo various types of reaction, e.g. unimolecular decomposition, dimerization or reaction with solvent. One type of reaction, when the decomposition of the species is first order or pseudo first order, is of interest. This is the case represented as:



A single sweep cyclic voltammetry for the system represented by equations 1 and 2 gives the idea of the stability of  $R$ . The rate of decomposition ( $k$ ) can be evaluated by measuring the ratio of anodic and cathodic peak at various scan rates,<sup>1-3</sup> or else by invoking Nicholson-Shain equation.<sup>2,4,5</sup>

If the reaction is fast, i.e.  $k = 10 \text{ sec}^{-1}$  (or higher) the method of peak current ratio  $(ip)_a/(ip)_c$  becomes less reliable since this ratio becomes less than 0.4 and hence difficult to measure.<sup>2</sup> The Nicholson-Shain equation can be used instead, provided  $E_{1/2}$  for the process given in equation (1) is already known. Then from peak potential,  $E_{1/2}$  and the sweep rate, the correct order of magnitude for  $k$  may be obtained.

Kosower and his coworkers proposed a method of calculating the rate constant ( $k$ ) by extending the current measurements at potential further away from first reduction peak and looking for the appearance of product and its reduction peak. This process is represented as



It is clear from equations (1-4) that, step (3), i.e. dimerization of  $A$ , being fast, step (2) is the rate-limiting and the rate of appearance of  $A_2$  and (hence  $A_2^{ne}$ ) depends upon  $k$ . Thus the ratio of cathodic peak currents of  $A_2^{ne}$  and  $R$ , at various voltage sweep rate can give the approximate value of  $k$ .

Since there is always problem of establishing a baseline to evaluate cathodic peak height for  $A_2^{ne}$  (equation 4) the anodic peak height for  $A_2^{ne} \rightarrow A_2$  may be used instead. For a process given in equation (4) the anodic and cathodic current ratio should be unity. Thus a ratio of cathodic peak current as given in equation (1) to the anodic peak current as given in equation (4), at various scan rate, can give a more accurate value for  $k$ . In the present work the latter method is utilized to evaluate the rate of decomposition of 4NBCl<sup>-</sup> which is known to follow the process given in equations (1-4).

### Results and Discussion

At slow scan rate, e.g. 33 mV/sec or 80.6 mV/sec 4-NBCl exhibits two reduction peaks and one oxidation peak (Fig. 1). These peaks, as interpreted earlier<sup>1,4,5</sup> correspond to the reduction of 4-NBCl 4,4'-dinitrobenzyl (DNBB) and reoxidation of dinitrobenzyl anion (-1.50 V vs Ag/AgClO<sub>4</sub>). At this sweep rate the cathodic peak current  $(ic)_{4NBCl}$  for the process



and anodic peak current  $(ia)_{DNBB^-}$  for the process



have the same magnitude, i.e.  $(ic)_{4NBCl}/(ia)_{DNBB^-} = 1$  (Fig. 1, ref. 5).

At high scan rate, this ratio becomes smaller because the amount of DNBB produced within that time scale is less. Thus at 12 V/sec, the ratio is about 0.68 (Fig. 2). If it is assumed that 68% of 4NBCl<sup>-</sup> decomposed in the time the voltage was swept from the  $E_p$  of 4NBCl<sup>-</sup> to  $E_p$  of DNBB (at 12 V/sec) a rate constant for the decomposition of 4-NBCl of about  $50 \text{ sec}^{-1}$  is obtained. This rate constant is close to the one reported earlier<sup>8</sup> and we believe to be more accurate. Hawley *et al.*<sup>5</sup> have reported a rate constant about  $(0) 10^4 \text{ sec}^{-1}$ , which is substantially higher than the one reported here. The value reported by Hawley are, most probably wrong, at least to two order of magnitude, e.g. Hawley reported a calculated value of rate constant for the

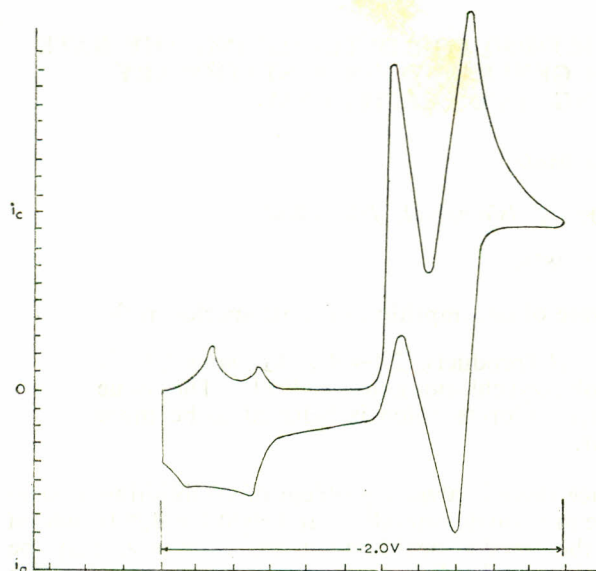


Fig. 1. Cyclic voltammogram of 4-NBCl in acetonitrile (0.1 M tetrabutyl ammonium perchlorate) at scan rate 33 mV/sec.

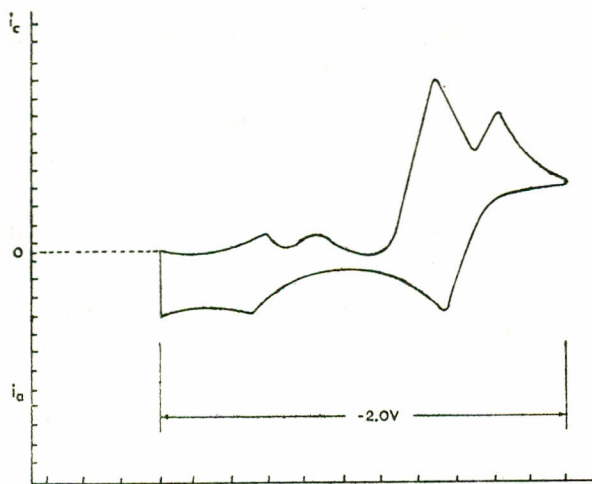


Fig. 2. Cyclic voltammogram of 4-NBCl in acetonitrile (0.1 M tetrabutyl ammonium perchlorate) at scan rate 12 V/sec.

decomposition of 4-NBBr<sup>-</sup> (4-nitrobenzyl bromide anion) of the order of (0) 10<sup>8</sup> sec<sup>-1</sup> while in fact direct experimental measurement has shown its value to be much smaller,<sup>7</sup> i.e. (0)10<sup>4</sup> sec<sup>-1</sup>. Hawley had calculated the rate constant invoking Nicholson and

Shain equation<sup>2</sup>, and using  $\sigma$ - $\rho$  relationship for evaluating  $E_{1/2}$ . Approximations in deriving the Nicholson-Shain equation and in evaluating  $E_{1/2}$  (by  $\sigma\rho$  relationship) can easily throw the value for  $k$  by two order of magnitudes. In fact rate constant for the reaction between 4-NBCl and pyridinyl radical as calculated electrochemically using Nicholson and Shain equation has shown that this method gives the rate constant at least one order of magnitude higher.<sup>6</sup>

At the same time the method reported here is also not flawless. The rate constant depends critically upon the ratio of the peak height, which depends upon the accurate determination of base-lines. It is not easy to ascertain the current peak ratio with the accuracy better than 10%. This means an error of 30% can incur in the rate constant. A more realistic value of the rate constant calculated here will be  $75 \pm 25$  sec<sup>-1</sup> which comes very close to the value reported by Hawley *et al.*<sup>5</sup> if a correction of two order of magnitude is made in the values for  $k$  reported by them.

### Experimental

Instruments used here have already been mentioned,<sup>1,8</sup> A flip-flop circuit was used for single sweep and every sweep was carried out on fresh mercury drop of hanging mercury drop electrode. Other experimental details have already been mentioned.<sup>8</sup>

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