TABLE I

[NaBr]/mol dm^{-3}	$\left[\begin{array}{c}\text{\small O}\end{array}\right]$/mol dm^{-3}	k'/s^{-1}	k/mol^{-1}dm^{3}s^{-1}
0.01	0.14	11	75
0.01	0.28	19	66
0.01	0.70	50	71
0.005	0.14	9	61

It was found that the average value of k is about 68 mol^{-1}dm^{3}s^{-1}

References:

(1) Jones, D.G., and Imperial Chemical Industries Ltd. Brit. patent 595041; C.A. 42 (1948) 2992.

(2) N. Clauson-Kaas, F. Limborg, and K. Glens, Acta Chemica Scandinavica, 6, (1952) 531.

(3) M. Fleischmann, F. Lasserre, J. Robinson and D. Swan, J.Electroanal.Chem., 177 (1984) 97.

# THE REDUCTION OF FORMALDEHYDE IN CONCENTRATED SOLUTIONS USING MICROELECTRODES

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Recently, there has been a considerable interest in the hydrodimerisation of formaldehyde to ethylene glycol (1,2). This process occurs at high concentrations of formaldehyde and the cathodic reaction occurs by the mechanism

$$CH_2(OH)_2 \rightleftharpoons HCHO + H_2O$$

$$2HCHO + 2e \longrightarrow \begin{array}{c} CH_2OH \\ | \\ CH_2OH \end{array}$$
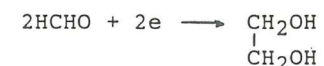
where the dehydration reaction is the rate determining step.

The Electrosynthesis Company has developed a very efficient process (3) and the recommended conditions include a low methanol content formate electrolyte, pH 5-7, containing a tetraalkylammonium salt, a high formaldeyde concentration (40 %), a high temperature (80ºC) and a cathode chosen from a range of carbons.

We have carried out a study of formaldeyde reduction at microelectrodes in conditions as close as possible to the Electrosynthesis Company's process. However, since it is not possible to manufacture carbon microelectrodes with surfaces which can be demonstrated to have the properties necessary for production of ethylene glycol in good yield, most of the experiments have employed mercury microelectrodes.

i-E curves were recorded for a concentration range from 0.04 to 40% in formaldehyde and for a range of temperatures. Figure 1 shows a typical i-E curve for 40% concentration on formaldehyde at room temperature.
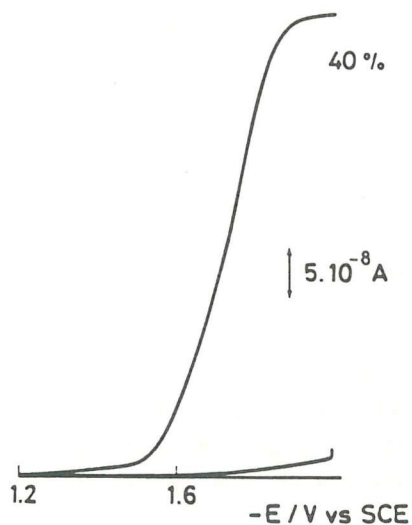
Figure 1. i - E curve at a Hg plated Au microdisc electrode (diameter 10 um) for the reduction of formaldehyde 40% in 1 mol dm^{-3} sodium formate at room temperature. Potential scan rate: 50 mV/s.

For the concentration range studied, the limiting current densities are always low compared to the diffusion limited current calculated from the expression

$$I = 4nFDc \ / \ r$$

where D is the diffusion coefficient, c the bulk concentration and r the radius of the microelectrode.

Clearly, the reduction of formaldehyde is always kinetically controlled, largely due to the slow dehydration of formalin.

Finally, the effect of increasing the temperature was studied. Well formed reduction waves were obtained for the reduction of 40% formaldehyde at temperatures between 15 and 90ºC. A strong increase in the limiting current density with temperature was observed, as shown in figure 2. Also shown in

the figure as a dashed line is the variation of the diffusion limited current density with temperature, calculated assuming that D = 5x10^{-6}cm^{2}s^{-1} at 20ºC, and that the energy of activation for diffusion is 8 kJ/mol.
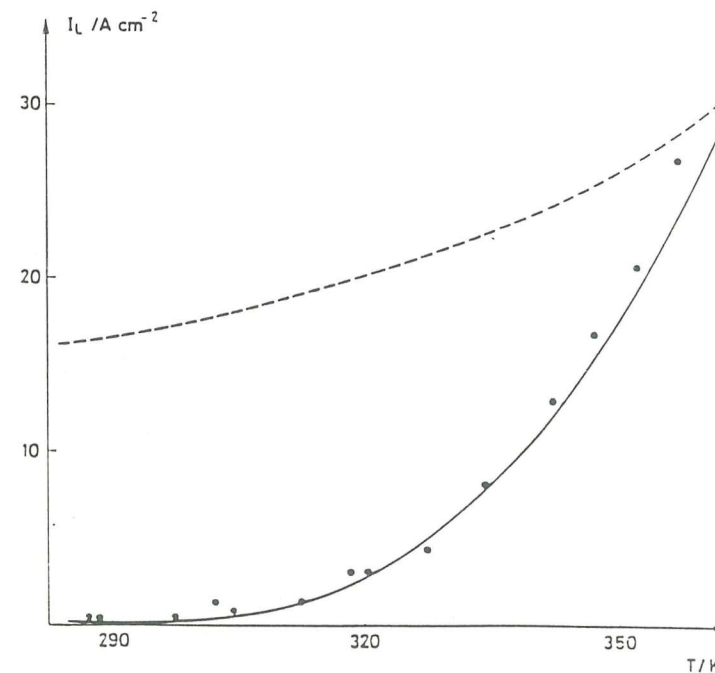

Figure 2. Dependence of the limiting current density for 40% formaldehyde reduction on temperature. The dashed line indicates the calculated mass transport limited current.

It can clearly be seen that the observed limiting current density approaches the calculated diffusion limited current density with increasing temperature and by 363K the difference is less than 10%. Hence, at this temperature the reduction of formaldehyde is close to diffusion controlled and, therefore, i_L/c should be proportional to n. Figure 3 shows a plot of i_L/c vs c which shows the change from a 2 electron to a 1 electron process.
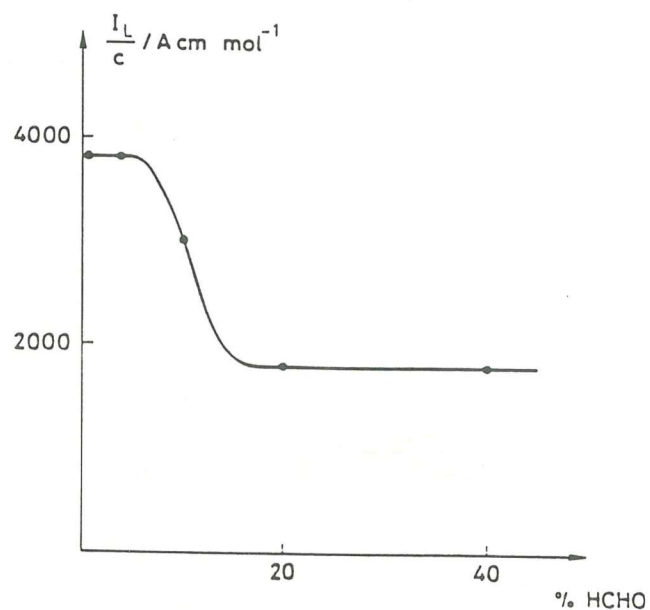
Figure 3. i_L/c as a function of % HCHO. Temperature 363K.

It can, thus, be concluded that, at high concentrations of formaldehyde the product is ethylene glycol and at low concentrations is methanol. These results confirm the necessity of using a high concentration of formaldehyde and demonstrate clearly the advantage of using an elevated temperature.

(1) H. Watanabe and M. Saito, Tokyo Soda Kenkyo, Hokoku, 24, (1979), 93.

(2) M. Saito and J. Tokuyuma, German Patent, (1980), 3,018,844.

(3) N. L. Weinberg, US Patent, (1984),4, 478,694.

ELECTROANALYTICAL DETERMINATION OF DIAZINON: DIFFERENTIAL PULSE POLAROGRAPHY AND ADSORPTIVE STRIPPING VOLTAMMETRY

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Diazinon, O,O-diethyl O-(2-isopropyl-6-methyl-4-pyrimidinyl) phosphorotioate, is a non-systemic organophosphorated pesticide frequently used againts aphids and larvae.

Diazinon shows, a relatively long residual action and is effective as a control of soil, fruit, vegetable and rice insects, is also useful for the control of pest in household and on livestock.

The reported electroanalytical methods (1,2) for the determination of diazinon present a detection limits of 2.0 p.p.m., a high value for the determination of this pesticide in residues. In this work two methods are proposed for its determination by differential pulse polarography, DPP, (detection limit: $2.65 \cdot 10^{-6}$ M) and by adsorptive stripping voltammetry, AdSV, (detection limit: $4.01 \cdot 10^{-9}$ M).

Reagents and solutions. Stock solutions of pure diazinon were prepared by dissolving the compound in methanol. The solutions were stored in the dark to mininise the risk of decomposition. The supporting electrolytes were Britton-Robinson buffer 0.12 M and acetate buffer 0.10 M. Alls chemicals used were of analytical-reagent grade.

Apparatus. A Metrohm Polarecord E-506, equipped with an E-505 stand, was employed. In DC and DPP techniques, a three-electrode system was used, the working electrode being a dropping-mercury electrode (DME). The reference electrode was a saturated calomel electrode and the counter electrode was a platinum wire. Highly purified nitrogen was passed through the solution to remove dissolved oxigen. For the adsorptive stripping voltammetry study the working electrode was Metrohm EA-290 hanging mercury electrode.

Polarographic study. In aqueous-methanolic medium and with Britton-Robinson buffer as supporting electrolyte, the pesticide shows a reduction wave (DC) or peak (DPP) whose currents are function on the percentage of methanol (MeOH) and the time elapsed between preparation and measure of the solutions. At a MeOH percentage of 40 % (v/v) the polarographic current is stable for a minimum of 60 minutes.