

# A KINETIC STUDY OF OXIDATION OF 1,2-DIOLS WITH PERIODIC ACID BY MEANS OF CURRENTLESS $E-t$ CURVES\*

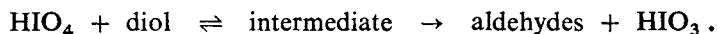
Vladimír DLASK

*Department of Physical Chemistry,  
Institute of Chemical Technology, 532 10 Pardubice*

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The oxidations of ethanediol, 1,2-propanediol, and 1,2-cyclohexanediol with periodic acid have been followed on various electrodes by means of the currentless potential-time curves, and the rate constant values found have been compared with the results obtained by the polarographical method.

The reaction between periodic acid and 1,2-diols has already been studied<sup>1-11</sup> and is known to proceed according to the following mechanism:



The overall reaction is of the second order, being first order in each periodic acid and diol. Therefore, it is possible to determine its rate constant by means of the earlier described method<sup>12</sup> of currentless potential-time curves and to compare the results obtained with those of other independent methods, which is the aim of the present communication.

## EXPERIMENTAL

### Reagents

If not otherwise stated, the chemicals are from Lachema Brno. Periodic acid *p.a.*, Feinchemie K.-H. Kalies KG: Aqueous solution of 0.1M-HIO<sub>4</sub> was prepared, and its factor was determined iodometrically in neutral medium (10% NaHCO<sub>3</sub> solution) by titration with standard sodium thiosulphate solution. The factor was checked periodically after several weeks, and it did not change. Ethyleneglycol *p.a.*, Reanal Budapest. Its purity was checked by elemental analysis: calculated: 38.70% C, 9.74% H; found: 38.60% C, 9.70% H. 1,2-Propanediol, tech. Chemical Works of W. Pieck, Nováky. It was purified by distillation, and the content of 99.9% of the

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compound was determined by the hydroxyl number. 1,2-Cyclohexanediol tech. BASF. It was purified by repeated crystallization (from an ethanol-ether mixture and from benzene) and checked by elemental analysis: calculated: 62.04% C, 10.41% H; found: 62.02% C, 10.30% H. These diols were dissolved in water to give 0.1M solutions whose factors were determined by re-titration of excess standard periodic acid iodometrically in neutral medium (10% NaHCO<sub>3</sub> solution) with standard sodium thiosulphate solution. Potassium iodide *p.a.* Sodium thiosulphate crystalline *p.a.* Solution of 0.1M-Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> in water was standardized with the use of potassium dichromate. Hydrochloric acid *p.a.*, potassium dichromate *p.a.*, sodium hydrogen carbonate *p.a.*, acetic acid *p.a.*, sodium acetate *p.a.*, sodium carbonate crystalline pure, mercury for polarography, Lachema, Chemapol Prague, anhydrous sodium sulphate *p.a.*

### Apparatus

The reactions were carried out in a discontinuous reactor<sup>13</sup>. The following indication electrodes were used: glossy platinum electrode, rotation ground gold electrode, platinum and carbon electrodes. The carbon ground electrode did not give reproducible results. A saturated calomel electrode with bridge was used as the reference electrode. The reaction vessel was protected against light<sup>10</sup>. The polarographical measurements were carried out with a Radelkis OH 102 apparatus using a tempered black-coated Kalousek vessel with separated mercurousulphate electrode.

### Registration of the *E-t* Curves

All the measurements were carried out in acetate buffer (pH 4.8) (ref.<sup>14</sup>). The 0.1M diol solution (1 or 2 cm<sup>3</sup>) was added to 25 cm<sup>3</sup> buffer solution, and, after attaining the required temperature, 0.1M periodic acid was added in such way that the parameter  $n \equiv [\text{HIO}_4]_{t=0}/[\text{diol}]_{t=0}$  was changed from 0.1 to 1.0 by 1/10 steps. The electrodes were washed with distilled water between the individual measurements. The glossy platinum electrode was immersed in acetate buffer after the measurement was finished. The initial concentrations were 0.0154 mol l<sup>-1</sup> for ethanediol and 0.083 mol l<sup>-1</sup> for 1,2-propanediol and 1,2-cyclohexanediol.

### Polarographical Measurements

The current-time dependence was registered with a polarograph with the applied voltage  $E = -0.400$  V. For the measurement, 50 cm<sup>3</sup> buffer was pipetted in the Kalousek vessel, tempered at 25°C, the periodic acid solution was added thereto, and oxygen was removed by bubbling through argon. When the current was stabilized, the polarograph recorder was started, and the diol solution was added. Its initial concentration was 0.001 mol l<sup>-1</sup> for ethanediol and propanediol, and 0.0005 mol l<sup>-1</sup> for cyclohexanediol.

## RESULTS AND DISCUSSION

The rate constants were determined from the sets of the currentless potential-time curves by application of the graphical-numerical method given in ref.<sup>12</sup>. The golden ground electrode only exhibited ideal behaviour in the oxidation of ethanediol (Fig. 1), whereas non-ideal behaviour was observed during the oxidations of propanediol and cyclohexanediol. The ground platinum electrode showed non-ideal behaviour in the oxidations of all three diols. With both these electrodes extremes

were found in the  $t(1 - n) \sim \log n$  dependence. The rate constants found are given in Table I. The glossy platinum electrode did not give satisfactory results, the anomalies observed being probably due to changes of the electrode surface. The  $E-t$  curves obtained from the measurements with the ground carbon electrode were quite irreproducible.

TABLE I

Values of the rate constants ( $\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$ )

Diol	Ground gold electrode	Ground platinum electrode	Polarographical method	Thermometry (ref. <sup>15</sup> )
Ethanediol	$2.99 \pm 0.41$	$2.78 \pm 0.29$	3.2	$3.12 \pm 0.14$
Propanediol	$13.86 \pm 0.92$	$16.51 \pm 1.48$	16.7	$14.27 \pm 0.27$
Cyclohexanediol	$33.68 \pm 0.96$	$39.05 \pm 1.06$	36.5	$36.76 \pm 0.86$

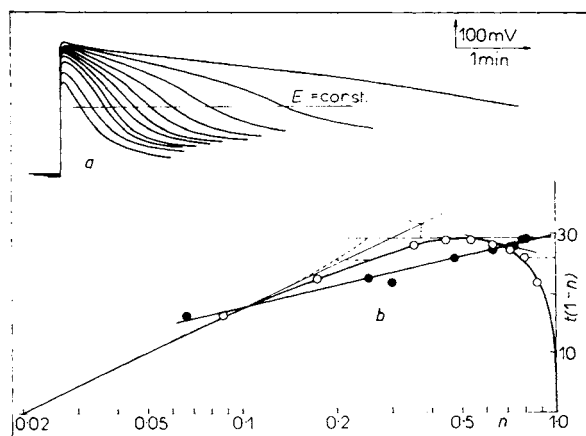


FIG. 1

Oxidation of 1,2-propanediol with periodic acid. *a*) The  $E-t$  curves with the  $n$  parameters: 0.087, 0.175, 0.262, 0.35, 0.438, 0.525, 0.613, 0.701, 0.788, 0.876, 0.963. The ground gold reaction electrode — s.c.e., medium:  $17 \text{ cm}^3$  buffer pH 4.8 ( $J = 1$ ),  $T = 298 \text{ K}$ ,  $[1,2\text{-propanediol}]_{t=0} = 0.01343 \text{ M}$ . The time was read at the potential level denoted as  $E = \text{const.}$  *b*) The values  $n_{\text{ex}} = 0.5$ ,  $n_0 = 0.02$ ,  $n_2 = 0.58$  were read from the  $t(1 - n) \sim \log n$  dependence (empty circles). Therefrom it was found  $\Theta = 2.04$ ,  $D/\beta = 4.32$ ,  $n_{-1} = 0.62$ ; graphically found value  $\Theta = 1.96$ , and, after linearization (full circles), the rate constant  $k$  was determined. The values used for the linearization were  $n = 0.087, 0.175, 0.35, 0.438, 0.525, 0.613, 0.701, 0.788, 0.876$

In the independent polarographic method, the concentration–time curves were linearized on the basis of kinetic equations of the II. order. The rate constants were determined from the slope of the straight line obtained from three linearized concentration–time dependences. The results are given in Table I.

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