

# Kinetic study of the oxidations with Ce(IV) ions by means of the dropping mercury, rotating platinum, and vibrating platinum electrodes

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In this paper the results of the kinetic measurements of the oxidation of hydrazine with Ce(IV) ions obtained polarographically by using the dropping mercury, rotating platinum, and vibrating platinum electrodes are compared and, on the other hand, the results of polarographic kinetic measurements are confronted with the results obtained spectrophotometrically. These comparisons show good agreement between the measured values of the rate constants and activation parameters (activation enthalpy  $\Delta H^\ddagger$  and activation entropy  $\Delta S^\ddagger$ ) obtained by independent procedures. The most accurate results in the polarographic procedures were obtained by using the vibrating platinum electrode.

In a series of papers [1–6] we studied kinetically the redox reactions of Ce(IV) ions on the basis of the time dependence of the limiting diffusion current of Ce(IV) ions. In these investigations we used the dropping mercury electrode as an indication electrode. Since the Ce(IV) ions (in a 0.1 M solution of sulfuric acid) show a half-wave potential  $E_{1/2} = +0.870$  V against the potential of saturated calomel electrode [7], mercury is not quite indifferent with respect to Ce(IV) ions. When using a sufficiently high concentration of sulfuric acid (at least 0.2 M), this reaction is slow and does not interfere with the reaction under study. Nevertheless, the catalytic effect of mercury on the investigated reaction is not *a priori* out of the question. In order to justify the use of the dropping mercury electrode for the kinetic investigation of the oxidations with Ce(IV), we studied the oxidation of hydrazine with Ce(IV) ions as a model reaction by using the dropping mercury, rotating platinum, and vibrating platinum electrodes. Besides this, the aim of this study is to compare the accuracy of the measured values of the rate constants and activation parameters — activation enthalpy  $\Delta H^\ddagger$  and activation entropy  $\Delta S^\ddagger$  — measured by different procedures.

## Experimental

The polarographic kinetic measurements of the redox reaction of Ce(IV) ions with hydrazine hydrogen sulfate were performed by recording the time dependence of the limiting diffusion current of Ce(IV) ions at the potential of  $-0.3$  V against the potential of the 1 M mercury(I) sulfate electrode by means of an LP 60 polarograph. The dropping mercury, rotating platinum, and vibrating platinum electrodes served as indication electrodes. The dropping mercury electrode had the following constants: flow rate  $m = 0.896 \times 10^{-3}$  g s<sup>-1</sup>, drop time  $t = 3.1$  s, at  $h = 50$  cm in currentless state. The

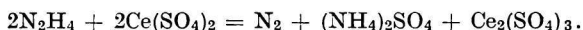
rotating platinum electrode 10 mm long and 0.5 mm in diameter was sealed into glass and coupled with a motor of the type M 22, Radiometer, with the constant frequency of revolutions (600 revolutions per minute). The vibrating platinum electrode was of equal dimensions as the rotating platinum electrode and was vibrated in horizontal direction with the frequency of 50 Hz by means of a vibrator. The Kalousek vessel with a separated 1 M mercury(I) sulfate electrode served as an electrolytic vessel. This cell was equipped with a jacket thermostatted by means of a Höppler ultrathermostat which kept a constant temperature accurate to  $\pm 0.05^\circ\text{C}$ .

The spectrophotometric kinetic measurements were performed on a Specord UV-VIS (Zeiss, Jena) spectrophotometer.

The chemicals used were of anal. grade. The solutions were prepared by dissolving the chemicals in redistilled water.

### Results and discussion

The redox reaction of Ce(IV) ions with hydrazine is first order with respect to the concentration of Ce(IV) ions and of hydrazine [8]. The reaction stoichiometry is expressed by the following equation



The rate constant ( $\text{s}^{-1}$ ) was always measured on the basis of the time dependence of the limiting diffusion current of Ce(IV) ions in a solution of 1 M- $\text{H}_2\text{SO}_4$  at  $2 \times 10^{-3}$  M- $\text{Ce}(\text{SO}_4)_2$  and  $3 \times 10^{-3}$  M- $\text{N}_2\text{H}_4$  by using the kinetic equation of the first-order reaction

$$k t = \ln i_0/i, \quad (1)$$

where  $i_0$  is the diffusion current of Ce(IV) ions at the beginning of the reaction and  $i$  is its value at a given moment of reaction. The investigated reaction obeyed the above equation at least in the period of the first two halfives. The rate constant was evaluated graphically from the slope of the above relationship. The standard deviation was always determined from ten individual measurements by means of the relationship

$$\delta = \frac{\Sigma \Delta i^2}{n(n-1)}, \quad (2)$$

where  $\Delta i$  is the difference between the arithmetic mean and individual measured value and  $n$  is the number of measurements.

Similarly we proceeded in the kinetic spectrophotometric measurements based upon the time dependence of the absorbance at the wavelength of 384 nm. The average values of the rate constant at  $20^\circ\text{C}$ , the standard deviations of individual measurements, and those of the means of measurements obtained by the methods used are presented in Table 1.

The activation parameters, *i.e.* the activation enthalpy  $\Delta H^\ddagger$  and activation entropy  $\Delta S^\ddagger$  were calculated by using the Eyring equation in the form

$$-\ln \frac{\bar{k} h}{k T} = \frac{\Delta H^\ddagger}{R T} - \frac{\Delta S^\ddagger}{R}, \quad (3)$$

where  $\bar{k}$ ,  $k$ , and  $R$  stand for the average value of the rate constant at the temperature  $T$  (K), the Boltzmann constant, and the gas constant, respectively. The activation parameters

Table 1

Values of the rate constants and their standard deviations  
determined by different procedures

Procedure	Rate constant (s <sup>-1</sup> ) at 20°C	Standard deviation of the mean [%]
By means of the dropping mercury electrode	$1.22 \times 10^{-2}$	1.7
By means of the rotating platinum electrode	$1.25 \times 10^{-2}$	2.0
By means of the vibrating platinum electrode	$1.19 \times 10^{-2}$	0.5
By spectrophotometric method	$1.21 \times 10^{-2}$	2.0

Table 2

Values of the activation parameters of the investigated reaction  
determined by different procedures

Procedure	$\Delta H^\ddagger$ [kcal mol <sup>-1</sup> ]	$\Delta S^\ddagger$ [cal mol <sup>-1</sup> K <sup>-1</sup> ]
By means of the dropping mercury electrode	$12.9 \pm 0.3$	-24
By means of the rotating platinum electrode	$12.7 \pm 0.6$	-24
By means of the vibrating platinum electrode	$12.9 \pm 0.2$	-24
By spectrophotometric method	$12.9 \pm 0.4$	-24

were evaluated graphically by the method of least squares, four values obtained for each rate constant at the temperatures of 5, 10, 15, 20, 25, and 30°C being always used for these calculations. For comparison, Table 2 presents the activation parameters measured by individual procedures. The deviation of activation enthalpy was determined from the graphical relationship  $\ln \bar{k} h/kT = f(1/T)$  using the formula [9]

$$\delta = 4.57 \sqrt{\frac{\sum (\log k_i/k_e)^2 n}{(n-2) \left[ \sum \frac{1}{T^2} - n \sum \frac{1}{T^2} \right]}}, \quad (4)$$

where  $k_i$  is the interpolated value of the rate constant,  $k_e$  is its experimental value, and  $n$  is the number of points.

The obtained results show that the dropping mercury electrode may be used reliably for the kinetic study of the mentioned redox reactions of Ce(IV) ions because the values of the rate constants and activation parameters are in accord with the values of these quantities measured by means of the rotating platinum and vibrating platinum electrodes or by the spectrophotometric method. In the mentioned electrochemical procedures the most accurate results were obtained by means of the vibrating platinum electrode. According to electrochemical literature the reproducibility of the results obtained by the use of the dropping mercury electrode is higher than that of the results obtained by means of solid electrodes. When using solid electrodes, the hysteresis of the  $i = f(E)$

curves is usually observed, *i.e.* the shape of these curves depends on the direction of polarization. Our results agree with these observations because the kinetic measurements carried out by means of the rotating platinum and vibrating platinum electrodes were always based on the time dependence of the limiting diffusion currents at constant potential (in addition to this no metal deposition occurred). The advantage of the vibrating platinum electrode with respect to the investigation of the homogeneous reaction of Ce(IV) ions consists in the fact that it can be used both in static and in flow systems.

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