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MECHANISM AND REACTION RATE OF THE KARL-FISCHER TITRATION REACTION

PART III. ROTATING RING-DISK ELECTRODE MEASUREMENTS — COMPARISON WITH THE AQUEOUS SYSTEM

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ABSTRACT

A platinum disk-platinum ring electrode was used to investigate the oxidation of sulfur dioxide by iodine and triiodide in aqueous solutions. Contrary to methanolic solutions, where the monomethyl sulfite ion is the only oxidizable species, in aqueous solutions both the hydrogen sulfite ion and the sulfite ion can be oxidized. The reaction rate was generally so high, that the method for measurements of homogeneous second order reactions had to be used. At pH values > 5 , the reaction proceeded too fast to be measured reliably. In a solution "diluted" with ethanol (50% of weight), however, the reaction rate was within the range where a rotating ring-disk electrode can be applied to measure fast homogeneous reactions. At very low pH values both the first order calculation technique and the second order method could be used. The results with both methods were in fair agreement.

INTRODUCTION

The oxidation of a methanolic sulfur dioxide solution by electrolytically generated iodine and triiodide has been studied by means of potentiometry [1] and by means of a galvanodynamic technique for the measurement of pseudo-first order reactions with the rotating ring-disk electrode [2]. It was found that the monomethyl sulfite ion is the oxidizable species. This ion is formed from methanol and sulfur dioxide:



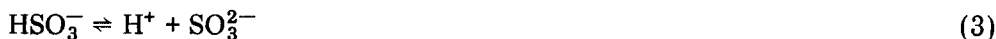
Both iodine and triiodide can oxidize the monomethyl sulfite, but the reaction rate constant of the iodine ($k_3 \approx 10^7 \text{ l}^2 \text{ mol}^{-2} \text{ s}^{-1}$) is much larger than that of the triiodide ion ($k_3 \approx 500 \text{ l}^2 \text{ mol}^{-2} \text{ s}^{-1}$). The reaction is first order in each of the reactants: CH_3SO_3^- , H_2O and I_2 (together with I_3^-) at relatively small water concentrations. When $c_{\text{H}_2\text{O}}$ exceeds 1 M, reaction becomes second order in

H₂O. This is most probably caused by the formation of hydrogen sulfite from sulfur dioxide and water:



Then, the hydrogen sulfite ion reacts further with iodine or triiodide and another water molecule.

In this part we have focussed our attention on the reaction between sulfur dioxide and iodine when the water concentration is very high, viz. in aqueous solutions. The reaction rate is now much higher than in methanolic solutions. Therefore, we had to use a calculation technique for the measurement of homogeneous pseudo-second order reactions. An important difference is that the mono-methyl sulfite cannot dissociate, while the hydrogen sulfite can:



Therefore, depending on the pH of the solution and the dissociation constants of the sulfurous compounds, the solution will contain sulfur dioxide, hydrogen sulfite or sulfite. The oxidation rates of these compounds with iodine and triiodide were investigated.

THEORY OF MEASUREMENT

Basically, the measurement of reaction rates with a rotating ring-disk electrode is the same for a second order reaction and for a first order reaction. The main differences exist in the galvanograms obtained and the evaluation of the results.

As is shown in Part II [2], the typical i_R vs. i_D curves for a first order reaction are straight lines through the origin with a slope N_k , for which:

$$0 \leq N_k = f(k_1/\omega) \leq N_0 \quad (4)$$

while the typical galvanograms for a second order reaction are curved. In a thorough study by Albery et al. [3,4], the measurement of second order reaction rate constants is based on the so-called titration curves, i.e. galvanograms where the reaction rate is very high compared to the diffusion rate. The difference between the titration curves and the experimental i_R vs. i_D curves enables us to calculate the rate constant. In the case of a very fast reaction between the iodine and triiodide formed at the disk electrode and the sulfurous compounds transported from the bulk of the solution by convective diffusion, no iodine and triiodide can enter into the solution, unless the disk current generates a flux of iodine and triiodide, larger than the transport limited flux of sulfurous compounds to the electrode. Assuming that the diffusion coefficients of the various species involved in the reaction are equal, the fluxes of the two reactants (in our case, iodine and triiodide and the sulfurous compounds, respectively) match, if the disk current equals a distinct value M , where

$$M = 0.62 \pi r_1^2 n F D^{2/3} \nu^{-1/6} \omega^{1/2} c_\infty \quad (5)$$

The symbols have the same significance as in Part II; c_∞ denotes the bulk concentration of the sulfurous compounds.

At larger values of i_D , there is a region near the disk where iodine and tri-

iodide can exist, but outside this region, only the sulfurous compounds can. The width of the boundary between the iodine region and the sulfurous region depends on the reaction rate: the slower the reaction, the more diffuse the boundary.

The "middle" of the boundary (where the concentrations of the iodine and triiodide and of the sulfurous compounds are equal) is just on the inside edge of the ring if i_D is set on a critical value by adjusting so that:

$$i_{D,k} = M / \{1 - F(\alpha)\} \quad (6)$$

where

$$\alpha = (r_2/r_1)^3 - 1 \quad (7)$$

and

$$F(\alpha) = \frac{\sqrt{3}}{4\pi} \ln \frac{(1 + \alpha^{1/3})^3}{1 + \alpha} + \frac{3}{3\pi} \arctan \left(\frac{2\alpha^{1/3} - 1}{\sqrt{3}} \right) + \frac{1}{4} \quad (8)$$

For a very fast reaction, no iodine and triiodide can reach the ring and the ring current will be zero, as long as $i_D \leq i_{D,k}$. If the reaction is not very fast, however, some iodine and triiodide can penetrate into the sulfurous region, so that at $i_D = i_{D,k}$, some iodine and triiodide penetrate across the inner edge of the ring. Then, there will be a ring current $i_{R,k}$:

$$|i_{R,k}| = 0.21 \pi r_2^2 n F D \nu^{-1/2} \omega^{3/2} k_2^{-1} \quad (9)$$

All we have to do, is to find the critical disk current and to measure the critical ring current at that point, in order to obtain the second order rate constant, k_2 .

One also can make use of the critical collection efficiency, N_k . Dropping the absolute value symbols for the sake of convenience, we can calculate with (5), (6) and (9)

$$N_k = \frac{i_{R,k}}{i_{D,k}} = \frac{0.34 r_2^2 D^{1/3} \{1 - F(\alpha)\} \omega}{r_1^2 \nu^{1/3} k_2 c_\infty} \quad (10)$$

At high disk currents, the galvanogram approaches the asymptote that can be described with

$$i_R = N_0 i_D - \beta^{2/3} M \quad (11)$$

where

$$\beta = (r_3/r_1)^3 - (r_2/r_1)^3 \quad (12)$$

An extrapolation of the i_R vs. i_D curve to $i_R = 0$, therefore, should give the value of M , but, especially at high rotation speeds or small reaction rate constants, the extrapolation is very unreliable. Instead, one could use (5) to calculate M , but c_∞ may differ at the end of a series of experiments from the initial value. Moreover, D stands for the diffusion coefficient of all species involved in the reaction, and some error is made if the diffusion coefficient of the triiodide ion is used. Therefore, it is usually preferable to follow a somewhat more elaborate procedure to find M .

It is possible to calculate the titration curve. If the disk current is such, that the reaction boundary is placed on the ring at r_1 , where

$$r_2 \leq r_j \leq r_3 \quad (13)$$

then, one can define a parameter β_j :

$$\beta_j = (r_j/r_1)^3 - (r_2/r_1)^3 \quad (14)$$

For $r_j = r_2$, $\beta_j = 0$ and for $r_j = r_3$, $\beta_j = \beta$, With this β_j corresponds a kinetic collection factor, N_j :

$$N_j = i_{R,j}/i_{D,j} = 1 - F(\alpha/\beta_j) - (1 + \alpha)(1 + \alpha + \beta_j)^{-1/3} \\ \times [1 - F\{(1 + \alpha + \beta_j) \cdot \alpha/\beta_j\}] \quad (15)$$

and a disk current, given by:

$$(i_{D,j}/M)^{-1} = 1 - F(\alpha) - \beta_j^{1/3}(1 + \alpha + \beta_j)^{-1/3} \\ \times [1 - F\{(1 + \alpha + \beta_j) \cdot \alpha/\beta_j\}] \quad (16)$$

Equations (15) and (16) describe a theoretical titration curve for a particular electrode. Although it is not possible to eliminate β_j from (15) and (16) to find $i_{D,j}/M$ as a function of N_j , one can easily obtain a graphical relationship by calculating $i_{D,j}/M$ and N_j for several β_j values ($0 < \beta_j < \beta$) and plotting the results (Fig. 1). To obtain M , we calculate the N_j values ($0 < N_j \leq N_0$) for several points of an experimental galvanogram. Then, we plot the corresponding experimental $i_{D,j}$ values against the theoretical $i_{D,j}/M$ values that we find with the aid of Fig. 1. A line through the origin and the points of the plot has a slope M . At high rotation speeds and low rate constants, the difference between the titration curve and the experimental galvanogram is the largest and therefore the points near the origin diverge from a straight line.

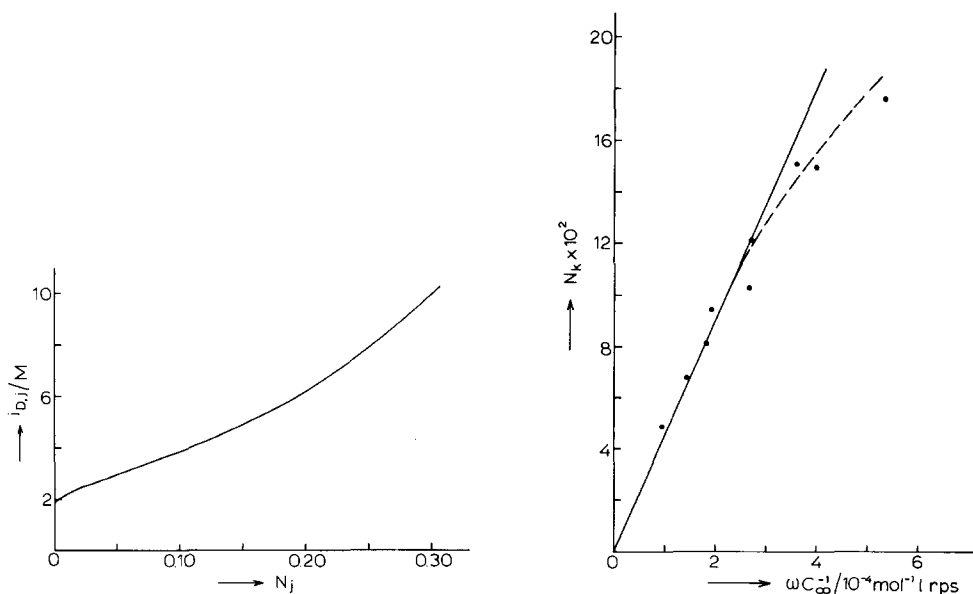


Fig. 1. Calculated dependence of $i_{D,j}/M$ on N_j for electrode no. 1.

Fig. 2. Dependence of the kinetic collection factor, N_k , on the ratio ω/c_{∞} (eqn. 10), water-ethanol (50–50), $c_{I^-} = 0.5 M$, $\text{pH} = 1.0$, $E_R = -0.2 V$ vs. SCE.

If M is found, one can calculate c_∞ with (5), if D and ν are known. This saves a titration afterwards. One also can find D if c_∞ is known. The critical disk current can now be calculated with (6). Like α , the factor $1 - F(\alpha)$ is an electrode parameter and is easily calculated. Some approximations, implied in the theory, demand that certain conditions must be met. For usual values of D and ν , it is necessary that

$$\omega/k_2c_\infty \ll 5 \quad (17)$$

and

$$(r_3 - r_2)/r_2 > 0.06(\omega/k_2c_\infty)^{3/5} \quad (18)$$

(A more precise formulation of these conditions can be found in the literature [5].) These conditions mean, that the rate constant of the reaction must not be too low and that the width of the ring must be large. These demands are quite opposite to those for a first order method. Figure 2 illustrates the validity of eqn. (10). At higher ω/c_∞ values the condition of eqn. (17) is broken.

EXPERIMENTAL

Distilled water and ethanol (Baker, A.R.) were used as solvents. The same reagents as described in the previous parts were used; for buffering also use was made of succinic acid (Merck, P.A.), malonic acid (Merck, P.A.), ammonium hydroxide (Baker, A.R.) and ammonium chloride (Baker, A.R.).

The same procedure is followed and the same equipment is used as is described in Part II. Only another electrode with a wide ring was needed for the second order method. The characteristics of the electrode used are given in Table 1. All experiments were performed at $25 \pm 0.3^\circ\text{C}$.

RESULTS AND DISCUSSION

We have tested our equipment by measuring the bromination of allyl alcohol in an aqueous solution. The rate constant of this reaction has been measured by Albery et al. [4], using the ring-disk electrode and by Bell and Atkinson [6],

TABLE 1
Characteristics of the electrodes no. 1 and 2

Characteristics	1	2
r_1/mm	2.017	2.011
r_2/mm	2.147	2.100
r_3/mm	3.028	2.201
α	0.2061	0.1387
β	2.1773	0.1723
$F(\alpha)$	0.4659	0.4143
$N_0(\text{theor.})$	0.4634	0.1595
$N_0(\text{exp.})^a$	0.465	0.157

^a Measured in a 0.5 M NaI solution in water-ethanol (50—50) at 25 rps.

TABLE 2

Values of k_2 for the bromination of allyl alcohol at different bromide concentrations
Number of experiments in parentheses

	$10^{-5} \times k_2 / \text{l mol}^{-1} \text{s}^{-1}$			
	$c_{\text{Br}^-} = 0.1 \text{ M}$	$c_{\text{Br}^-} = 0.2 \text{ M}$	$c_{\text{Br}^-} = 0.3 \text{ M}$	$c_{\text{Br}^-} = 0.4 \text{ M}$
Our experiments	3.06 (8)	1.92 (7)	1.39 (4)	1.42 (8)
Albery et al. [4]	2.76 (62)	1.95 (32)	1.62 (28)	1.42 (22)
Bell and Atkinson [6]	3.09	2.26	—	1.51

using low-concentration potentiometry. As shown in Table 2, the results of our measurements are in fair agreement with those of the other investigators. In Fig. 3, a typical galvanogram is shown for a second order reaction. The asymptote is drawn according to eqn. (11), after M has been calculated with the procedure outlined above. It is clear, that simply drawing a tangent to the galvanogram would have given an erroneous result. Usually, a low rotation speed is used to find M , because in that case, according to (9), the critical ring current is low and there is little difference between the (experimental) galvanogram and the (theoretical) titration curve. For the calculation of the rate constant, however, it is advantageous to use the higher rotation speeds and to expand the ring current scale (Fig. 4).

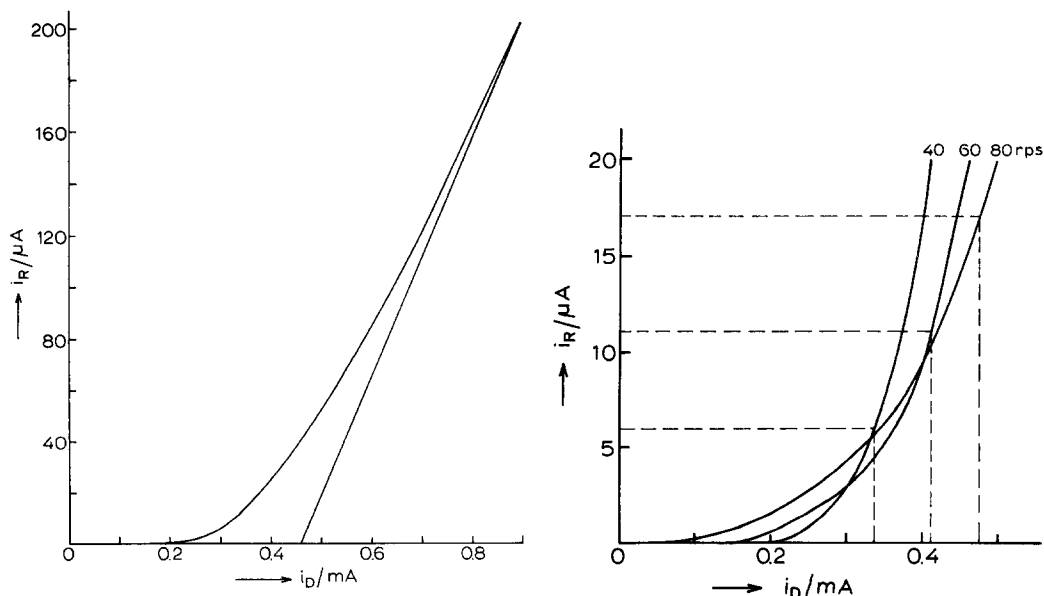


Fig. 3. Typical second order galvanogram. Electrode no. 1 in water-ethanol (50–50), $\omega = 20$ rps, $c_{\text{I}^-} = 0.5 \text{ M}$, c_{SO_2} (total) = 1.58 mM, pH = 2.1, $E_{\text{R}} = -0.2 \text{ V}$ vs. SCE.

Fig. 4. Kinetic curves of the system of Fig. 3 at 40, 60 and 80 rps.

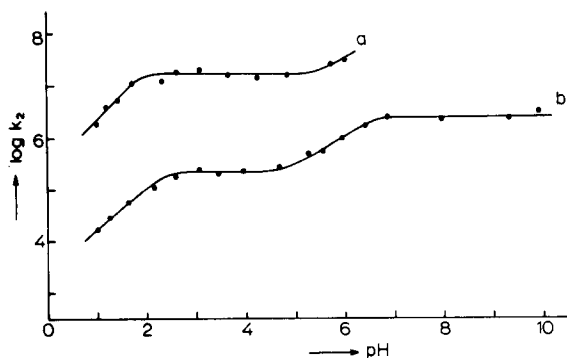


Fig. 5. Reaction rate constant as a function of pH. (a) 0.5 M NaI in water; (b) 0.5 M NaI in the water-ethanol mixture.

We can obtain the rate constant from the critical ring current with (9) or from the collection efficiency with (10), if we know ν and D . The viscosity coefficient was measured with an Ubbelohde viscosimeter; for an aqueous solution of 0.5 M NaI, we found $\nu = 8.7 \times 10^{-7} \text{ m}^2 \text{ s}^{-1}$. The diffusion coefficient was found, using eqn. (5). For that purpose, M was calculated with the procedure described above. Before and after the experiment, c_∞ was determined by an iodometric titration and the mean value was used for the calculations. We found for D a value of $9.8 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$. The pH dependence of the reaction rate in water is shown in Fig. 5a. The points in this Figure represent the mean of several measurements with different sulfur dioxide concentrations at a given pH value. Up to pH = 1.7, the logarithm of the reaction rate constant increases linearly with the pH. In the range from pH = 2.3 to pH = 5.2, the rate constant does not vary. At $c_{\text{T}} = 0.5 \text{ mol l}^{-1}$, we found $\log k_2 = 7.21 \pm 0.08$. At pH values larger than 5.2, the reaction rate increases again, but the reaction proceeds then too fast for accurate measuring.

As in methanolic solvents, it appears that not sulfur dioxide itself but a sulfurous base is oxidized. In water, this is the hydrogen sulfite ion. The first dissociation constant of sulfurous acid ($\text{p}K_{1a} = 1.8$ [7]) corresponds very well with the inflexion point of the $\log k_2$ vs. pH curve. The increase of the reaction rate at pH values larger than 5.2 must be attributed to the formation of the sulfite ion ($\text{p}K_{2a} = 6.9$ [7]), assuming that it reacts faster than the hydrogen sulfite ion.

To investigate the reaction with the sulfite ion, we have tried to lower the reaction rate by "diluting" the water with ethanol (50% of weight). We used ethanol instead of methanol because more data for ethanol-water mixtures are known. Moreover, this replacement does not alter significantly the relevant properties of the system.

The reaction rate decreased by about two orders of magnitude, so that the oxidation of the sulfite ion could be measured with the rotating ring-disk electrode. The viscosity coefficient and the diffusion coefficient were measured as with water as solvent: $\nu = 2.5 \times 10^{-6} \text{ m}^2 \text{ s}^{-1}$ and $D = 4.1 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$. The dissociation constants of sulfurous acid in the water-ethanol mixture (that also contained 0.5 M sodium iodide) were determined from a titration with sodium

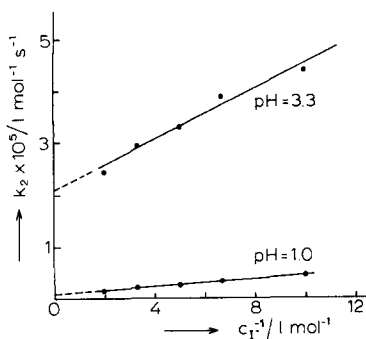


Fig. 6. Reaction rate constant in water-ethanol (50–50) as a function of the iodide concentration at pH = 1.0 and pH = 3.3.

hydroxide: $pK_{1a} = 2.3 \pm 0.1$ and $pK_{2a} = 7.0 \pm 0.2$.

The glass electrode-pH meter combination was calibrated with a 0.01 *M* perchloric acid solution and a 0.5 *M* acetic acid +0.5 *M* sodium acetate solution. The dissociation constant of the acetic acid was taken from the literature (5.84 [8]). In the pH range from 2.3 to about 5, the prevalent sulfurous species is the hydrogen sulfite ion. The rate constant of its oxidation in a 0.5 *M* iodide solution is given by $\log k_2 = 5.35 \pm 0.08$ (Fig. 5b). At pH values larger than 7.5 the prevalent sulfurous compound is the sulfite ion, for which we found $\log k_2 = 6.40 \pm 0.18$.

The reaction rate is dependent on the iodide concentration. In Fig. 6 this dependence is shown for the water-ethanol mixture. As has been pointed out in the previous parts, the intercept of the k_2 vs. $1/c_{I^-}$ curve equals $k_{I_3^-}$, the rate constant for the triiodide ion, while the slope of the curve equals k_{I_2}/K_s , the rate constant for iodine, divided by the stability constant of the triiodide ion. At pH = 3.3, where practically all the sulfur dioxide is converted into hydrogen sulfite, we found:

$$k_{I_3^-} = (2.09 \pm 0.15) \times 10^5 \text{ l mol}^{-1} \text{ s}^{-1}$$

and

$$k_{I_2}/K_s = (2.44 \pm 0.25) \times 10^4 \text{ s}^{-1}$$

We have measured K_s in the water-ethanol mixture, following the voltammetric method of Guidelli and Piccardi [9], and found:

$$K_s = (7.10 \pm 0.50) \times 10^3 \text{ l mol}^{-1}$$

so that

$$k_{I_2} = (1.73 \pm 0.29) \times 10^8 \text{ l mol}^{-1} \text{ s}^{-1}$$

It has not been possible to measure the dependence of the rate constant on the iodide concentration at pH >6, because at decreasing iodide concentrations the reaction rate increases so much, that it cannot any longer be measured with sufficient reliability.

At pH = 1.0, the reaction proceeds slow enough in the ethanol-water mixture

to measure its rate with the first order method as described in Part II, as well as with the second order method.

A thin gap-thin electrode had to be used for the (pseudo-) first order method. The calculated λ vs. N_k plot for this electrode is shown in Part II (electrode no. 2).

With the first order method, we found at pH = 1.2 and $c_{I^-} = 0.5 M$:

$$k_2 = (1.71 \pm 0.26) \times 10^4 \text{ l mol}^{-1} \text{ s}^{-1}$$

The result of the second order method was:

$$k_2 = (1.67 \pm 0.25) \times 10^4 \text{ l mol}^{-1} \text{ s}^{-1}$$

This close agreement is a good indication for the reliability of both methods. In Part II, it was shown, that with methanol as solvent and at low pH values, the formation of the relatively weak complex SO_2I^- had to be accounted for. The stability constant of this complex in water (0.38 l mol^{-1} [10]) and in the water-ethanol mixture (ca. 0.2 l mol^{-1} , measured spectroscopically in the way described in Part II) is so low, that no corrections had to be made.

CONCLUSION

In aqueous solutions, not sulfur dioxide, but the hydrogen sulfite ion and the sulfite ion are oxidized by triiodide and iodine, the sulfite ion having a higher rate constant than the hydrogen sulfite ion. Iodine reacts much faster than triiodide. So, there is a fair similarity between the reactions in aqueous solutions and in methanol.

The second order ring-disk method extends the range of rate constants that can be measured with the first order technique.

Employing both methods, it was possible with our system to measure a continuous range of second order rate constants from less than $10 \text{ l mol}^{-1} \text{ s}^{-1}$ up to $3 \times 10^7 \text{ l mol}^{-1} \text{ s}^{-1}$, using the same equipment. Only the electrodes for a first order method and a second order method are different.

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