

Hydrogen peroxide as an intermediate in electrocatalytic reduction of oxygen. A new method for the determination of rate constants

Citation for published version (APA):

Brink, van den, F. T. B. J., Barendrecht, E., & Visscher, W. (1980). Hydrogen peroxide as an intermediate in electrocatalytic reduction of oxygen. A new method for the determination of rate constants. *Journal of the Electrochemical Society*, 127(9), 2003-2006. <https://doi.org/10.1149/1.2130053>

DOI:

[10.1149/1.2130053](https://doi.org/10.1149/1.2130053)

Document status and date:

Published: 01/01/1980

Document Version:

Publisher's PDF, also known as Version of Record (includes final page, issue and volume numbers)

Please check the document version of this publication:

- A submitted manuscript is the version of the article upon submission and before peer-review. There can be important differences between the submitted version and the official published version of record. People interested in the research are advised to contact the author for the final version of the publication, or visit the DOI to the publisher's website.
- The final author version and the galley proof are versions of the publication after peer review.
- The final published version features the final layout of the paper including the volume, issue and page numbers.

[Link to publication](#)

General rights

Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

- Users may download and print one copy of any publication from the public portal for the purpose of private study or research.
- You may not further distribute the material or use it for any profit-making activity or commercial gain
- You may freely distribute the URL identifying the publication in the public portal.

If the publication is distributed under the terms of Article 25fa of the Dutch Copyright Act, indicated by the "Taverne" license above, please follow below link for the End User Agreement:

www.tue.nl/taverne

Take down policy

If you believe that this document breaches copyright please contact us at:

openaccess@tue.nl

providing details and we will investigate your claim.

REFERENCES

- D. G. Lovering and R. M. Oblath in "Ionic Liquids," D. G. Lovering and D. Inman, Editors, Plenum Press, New York (1981).
- D. G. Lovering, R. M. Oblath, and A. K. Turner, *J. Chem. Soc. Chem. Commun.*, 673 (1976).
- H. S. Swofford and H. A. Laitinen, *This Journal*, 110, 814 (1962).
- T. E. Geckle, Thesis, Penn. State University (1964); U.S.A.E.C., TID21511 (1964).
- M. Peleg, *J. Phys. Chem.*, 71, 4553 (1967).
- G. J. Hills and P. D. Power, *J. Polarogr. Soc.*, 13, 71 (1967).
- P. G. Zambonin, V. L. Cardetta, and G. Signorile, *J. Electroanal. Chem. Interfacial Electrochem.*, 28, 237 (1970); *Anal. Chem.*, 43, 1571 (1971).
- J. Jordan, *J. Electroanal. Chem. Interfacial Electrochem.*, 29, 127 (1971).
- A. Espinola and J. Jordan, in "Proceedings A.C.S. Symposium," San Francisco, August (1976).
- J. E. B. Randles and W. White, *Z. Electrochem.*, 59, 666 (1955).
- V. Sh. Palanker, A. M. Skundin, and V. S. Bagot-skii, *Elektrokhim.*, 2, 640 (1966).
- D. G. Lovering, Thesis, City University (1969); Extended Abstracts, p. 340, 23rd Meeting I.S.E., Stockholm (1972).
- D. G. Lovering, *Collect. Czech. Chem. Commun.*, 37, 3697 (1972).
- J. P. Frame, E. Rhodes, and A. R. Ubbelohde, *Trans. Faraday Soc.*, 57, 1075 (1961).
- J. Braunstein, *Inorg. Chim. Acta Rev.*, 2, 19 (1968).
- T. B. Tripp and J. Braunstein, *J. Phys. Chem.*, 73, 1984 (1969).
- P. G. Zambonin, *J. Electroanal. Chem. Interfacial Electrochem.*, 24, 365 (1970) et seq.
- D. Inman, D. G. Lovering, and R. Narayan, *Trans. Faraday Soc.*, 63, 3017 (1967).
- J. Dandoy and L. Gierst, *J. Electroanal. Chem.*, 2, 116 (1961).
- C. J. Liu, J. Hasson, and G. Pedro Smith, *Inorg. Chem.*, 7, 2244 (1968).
- S. V. Volkov and N. I. Buryak, *Zh. Neorg. Khim.*, 17, 1045 (1972).
- T. R. Griffiths and P. J. Potts, *Inorg. Chem.*, 14, 1039 (1975).
- M. Steinberg and N. Nachtrieb, *J. Am. Chem. Soc.*, 72, 3558 (1950).
- R. M. Oblath, Thesis, C.N.A.A. (R.M.C.S., Shrivenerham) (1978).
- G. C. Barket and R. L. Faircloth, A.E.R.E. Report C/R 2032 (1956).
- E. P. Parry and R. A. Osteryoung, *Anal. Chem.*, 40, 65 (1968).
- G. C. Barker and A. W. Gardener, *Z. Anal. Chem.*, 173, 79 (1960).
- H. Matsuda and Y. Ayabe, *Z. Electrochem.*, 59, 494 (1955).
- R. S. Nicholson and I. Shain, *Anal. Chem.*, 36, 706 (1964).
- Z. Galus, "Fundamentals of Electrochemical Analysis," Ellis Horwood, Chichester (1976).
- E. Eriksrud, *J. Electroanal. Chem. Interfacial Electrochem.*, 90, 347 (1978).
- L. R. McCoy, H. B. Mark, Jr., and L. Gierst, *J. Phys. Chem.*, 72, 4637 (1968), et seq.
- B. O. Field and C. J. Hardy, *Q. Rev.*, 18, 361 (1964); C. C. Addison, *Q. Rev.*, 25, 289 (1971).
- See D. G. Lovering, *Collect. Czech. Chem. Commun.*, 38, 1719 (1973), for discussion and further references.
- R. D. Shannon and C. T. Prewitt, *Acta Crystallogr. Sect. B*, 25, 925 (1969); *ibid.*, 26, 1076 (1970).

Hydrogen Peroxide as an Intermediate in Electrocatalytic Reduction of Oxygen. A New Method for the Determination of Rate Constants

F. van den Brink, E. Barendrecht,* and W. Visscher

Laboratory for Electrochemistry, University of Technology, 5600 MB Eindhoven, The Netherlands

ABSTRACT

On most electrocatalysts H_2O_2 is an intermediate in the electroreduction of oxygen. H_2O_2 can decompose either chemically or electrochemically and in assessing the performance of the electrocatalyst it is crucial to distinguish between these reaction paths. A simple method is proposed to determine whether or not the chemical path is followed.

For the electrochemical reduction of oxygen a general scheme of reactions can be given as in Fig. 1. Whether the reduction of oxygen to water will follow the direct path 1 or the consecutive path 2-3, or both these paths in parallel, is determined by the electrocatalytic properties of the electrode which are also critical for the further reaction of H_2O_2 : electrochemical reduction (reaction 3) and/or chemical decomposition (reaction 4).

With the introduction of the rotating ring-disk electrode technique it became possible to distinguish between the consecutive and parallel pathways (1-4). Here, the disk current is measured at various potentials and rotation frequencies, while simultaneously the ring current is measured at a potential at which

hydrogen peroxide is oxidized quantitatively. Several methods have been proposed to analyze the data obtained from these experiments; these methods have been reviewed by Pleskov and Filinovskii (5), while Wroblowa (6) has added a general criterion for distinguishing between the parallel and consecutive pathway. These analyses show that, in principle, only four (combinations) of the five rate constants in the general scheme can be obtained.

A problem which remains to be solved is that of the fate of the hydrogen peroxide, produced by reactor 2 in Fig. 1: H_2O_2 can be either reduced electrochemically (reaction 3) or chemically decomposed (reaction 4). Moreover, the solution of this problem is of vital importance in the evaluation of the performance of electrocatalysts for the oxygen electrode, since reaction 4 involves no net electron transfer and is

* Electrochemical Society Active Member.

Key words: electrocatalysts, reduction, decomposition.

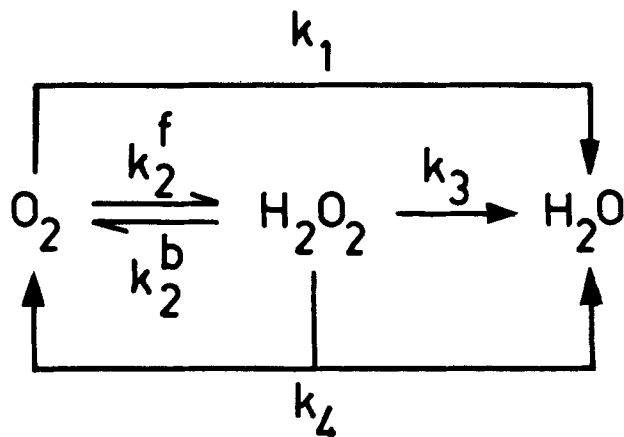


Fig. 1. Scheme of reactions for reduction of oxygen

electrochemically wholly unproductive. In this paper we will present a simple method to determine the rate constant of reaction 4, so that, in principle, it becomes possible to calculate all five individual rate constants of Fig. 1.

Theory

In the ring-disk electrode (RRDE) experiment, referred to in the introduction, sets of disk currents (I_D) and limiting ring currents (I_R) are obtained as functions of rotation frequency (ω) and disk potential, E_D . These data are analyzed by plotting at constant E_D according to (5)

$$-N_o I_D / I_R = A + B / \sqrt{\omega} \quad [1]$$

and

$$-N_o (I_{D, \text{lim}}^{\text{H}_2\text{O}_2} - I_D) / I_R = C + D \sqrt{\omega} \quad [2]$$

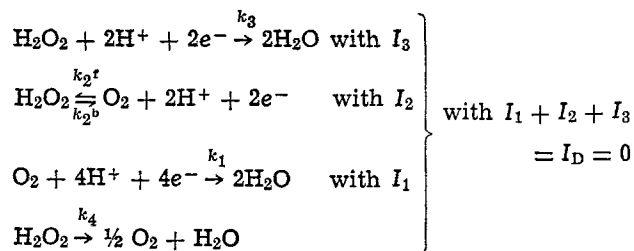
where $I_{D, \text{lim}}^{\text{H}_2\text{O}_2}$ is the limiting current at the disk for the reduction of oxygen to water and N_o is the RRDE's collection efficiency (7). A , B , C , and D are functions of the five rate constants, from which k_1 , k_2^f , $2k_2^b + k_4$, and $2k_3 + k_4$ can be obtained (5).

We wish to point out that the value of k_4 can be found in many practical cases by measuring ring currents in a solution containing only H_2O_2 and no O_2 , while the disk current is kept zero.

Relations between currents and rotation frequencies in H_2O_2 containing solutions have been derived by Bagotskii (1). From his equations the combinations $2k_2^b + k_4$, $2k_3 + k_4$, and $k_2^f - k_3$ can be obtained. A further extension of this method was given by Tarasevich and Radyushkina (8) who applied Bagotskii's equations under the condition that $I_D = 0$. They, again, found k_1 , k_2^f , $2k_2^b + k_4$ (describing the rate with which H_2O_2 gives O_2), and $2k_3 + k_4$ (describing the rate with which H_2O_2 gives H_2O). We will show that they lost valuable information, *viz.*, that obtained from the value of the disk's open-circuit potential, by substituting the zero current condition ($I_D = 0$) only in Bagotskii's resulting equations (1).

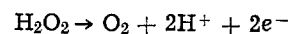
In a solution containing hydrogen peroxide, but no oxygen, the hydrogen peroxide will react electrochemically (reactions 2 and 3) and chemically (reaction 4), giving oxygen and/or water; oxygen may react further (reactions 1 and 2). The quantities of formed oxygen and of decomposed hydrogen peroxide can be determined by measuring the anodic and cathodic limiting currents on the ring electrode. If, moreover, the disk current is zero, the net amount of oxygen formed by the electrochemical reaction is known if the ratio of the rates of production and of consumption of O_2 by the electrochemical reactions, *i.e.*, $k_2^b - k_3 / 2k_1 + k_2^f$ is known at the disk's rest-potential. This means that the amount of oxygen formed by reaction 4 can be found, *i.e.*, that the value of k_4 can be determined.

Thus, on the disk electrode

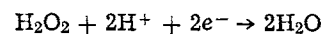


The assumptions are that reaction 4 is potential independent, that the pertinent reactions are first order in O_2 or in H_2O_2 , and that adsorption to and desorption from the electrocatalyst of O_2 and H_2O_2 are fast.

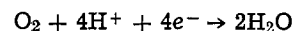
On the ring electrode the anodic limiting current is $I_{R, \text{lim}}^a$ for the reaction



and $I_{R, \text{lim}}^c$ the cathodic limiting current for the reactions



and



At the disk we have the mass balances, for hydrogen peroxide

$$\gamma_2 \sqrt{\omega} (c_2^s - c_2^o) = (k_{2,r}^b + k_{3,r} + k_4) c_2^o - k_{2,r}^f c_1^o \quad [3]$$

and for oxygen

$$\gamma_1 \sqrt{\omega} c_1^o = (k_{2,r}^b + \frac{1}{2} k_4) c_2^o - (k_{1,r} + k_{2,r}^f) c_1^o \quad [4]$$

Because of the zero current condition

$$\frac{I_D}{2FA} = (k_{2,r}^b - k_{3,r}) c_2^o - (2k_{1,r} + k_{2,r}^f) c_1^o = 0 \quad [5]$$

where the c 's are the concentrations of O_2 (subscript 1) and of H_2O_2 (subscript 2). The superscripts o and s on the c 's denote the electrode surface and the bulk of the solution, respectively, while a subscript r is attached to k_1 , k_2^f , k_2^b , and k_3 because the disk electrode is at its rest potential. Further, $\gamma \sqrt{\omega} = 0.62D^{2/3} \nu^{-1/6} \sqrt{\omega}$ is the rate constant for diffusion and A the disk area.

At the ring we have the limiting currents

cathodic

$$-\frac{I_{R, \text{lim}}^c}{N_o A F} = 4\gamma_1 \sqrt{\omega} c_1^o - 2k_4 c_2^o + \frac{\beta^{2/3}}{N_o A F} I_{D, \text{lim}}^{\text{H}_2\text{O}_2} \quad [6]$$

anodic

$$\frac{I_{R, \text{lim}}^a}{N_o A F} = -2k_4 c_2^o + \frac{\beta^{2/3}}{N_o A F} I_{D, \text{lim}}^{\text{H}_2\text{O}_2} \quad [7]$$

where $I_{D, \text{lim}}^{\text{H}_2\text{O}_2}$ is the absolute value of the limiting current at the disk for the oxidation of H_2O_2 to O_2 and $\beta^{2/3}$ is a geometrical factor, defining the shielding factor $(1 - N_o \beta^{-2/3})$ of the RRDE (7).

Elimination of c_1^o and c_2^o between the sets of Eq. [3], [4], and [6], and [3], [4], and [7], respectively, together with the condition [5] gives

$$\frac{I_{R, \text{lim}}^c}{2N_o A F c_2^s} = \frac{k_4}{1 + K} - \left(\frac{K}{1 + K} + \frac{\beta^{2/3}}{N_o} \right) \gamma_2 \sqrt{\omega} \quad [8]$$

and

$$\frac{-I_{R, \text{lim}}^a}{2N_o A F c_2^s} = \frac{k_4}{1 + K} - \frac{\beta^{2/3}}{N_o} \gamma_2 \sqrt{\omega} \quad [9]$$

where

$$K = \frac{2\gamma_1}{\gamma_2} \frac{k_{2,r}^b - k_{3,r}}{2k_{1,r} + k_{2,r}^f}$$

The pseudo constant k can be obtained by extrapolation of the values for the k 's found with Eq. [1] and [2] to the rest potential at each rotation frequency.

If we may assume that the rest potential will not vary strongly with the RRDE's rotation frequency, K will be a constant. Then the plots of the limiting ring currents *vs.* $\sqrt{\omega}$ will give straight lines. Two limiting cases can be considered (Fig. 2). First $K \ll 1$, i.e., H_2O_2 is, electrochemically, much less reactive than O_2 at the disk electrode. Therefore the anodic and cathodic limiting ring currents become equal, while reaction 4 is responsible for extra shielding of the ring current by the disk electrode. The second case $K \gg 1$, i.e., H_2O_2 is electrochemically more reactive. O_2 formed on the disk diffuses away, thereby increasing the cathodic limiting ring current. Now the influence of reaction 4 is much less than in the first case, because of the low H_2O_2 concentration near the disk surface. In Fig. 2, schematic diagrams are given for these two cases.

In general, by plotting $I_{R,\text{lim}}^a$ *vs.* $\sqrt{\omega}$, or, more precisely, $(1 + K)I_{R,\text{lim}}^a$ *vs.* $(1 + K)\sqrt{\omega}$ (Eq. [9]), c_2^s can be found. Then k_4 can be calculated at each value of ω from

$$k_4 = (1 + K) \left[\frac{I_{R,\text{lim}}^c}{2N_o A F c_2^s} + \left(\frac{K}{1 + K} + \frac{\beta^{2/3}}{N_o} \right) \gamma_2 \sqrt{\omega} \right] \quad [10a]$$

$$= (1 + K) \left[\frac{-I_{R,\text{lim}}^a}{2N_o A F c_2^s} + \frac{\beta^{2/3}}{N_o} \gamma_2 \sqrt{\omega} \right] \quad [10b]$$

The results can be averaged to give a final value of k_4 . Alternatively, k_4 can be determined from the intercepts of $(1 + K)I_{R,\text{lim}}^c/2N_o A F c_2^s$ and $-(1 + K)I_{R,\text{lim}}^a/2N_o A F c_2^s$ *vs.* $(1 + K)\gamma_2 \sqrt{\omega}$. The resulting value of k_4 is then subtracted from $2k_2^b + k_4$ and $2k_3 + k_4$, obtained from Eq. [1] and [2], to give the separate values for all five rate constants at each potential for which ring and disk currents are available.

Experimental

As an example, an experiment according to the line of reasoning described above was carried out, using an RRDE with an Au disk and a Pt ring in 1M KOH at 298°K. The construction of the RRDE was as described before (9). Its dimensions were such that $A = 51.5 \times 10^{-6} \text{ m}^2$, $N_o = 0.1437$, and $\beta = 0.1515$ (as calculated from the radii $r_{10} = 4.047 \text{ mm}$, $r_{20} = 4.260 \text{ mm}$, and $r_{30} = 4.437 \text{ mm}$). A standard electrochemical cell was used, with a reversible hydrogen electrode (RHE) as reference and a platinum wire as counter-electrode. The Pt ring was slightly platinized ($5 \times$

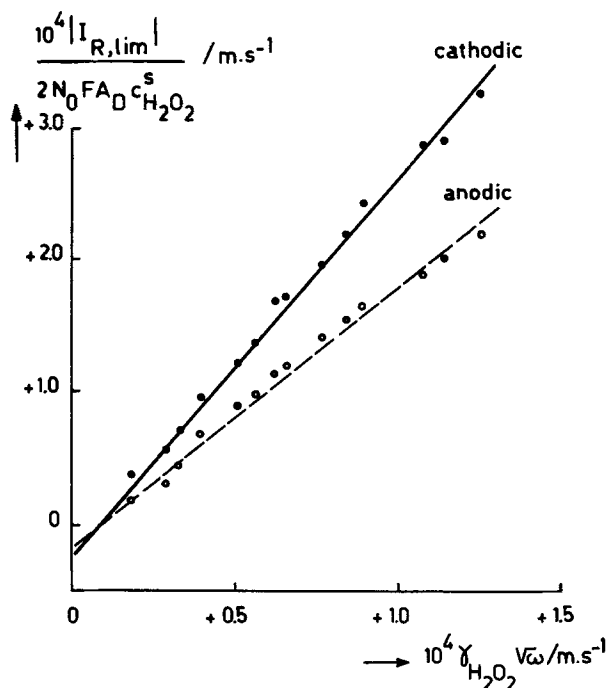


Fig. 3. Limiting ring currents *vs.* $\sqrt{\omega}$; for an Au/Pt-RRDE in 1N KOH at 298°K, plotted according to Eq. [8] and [9]. a = anodic, c = cathodic.

$10^{-6} \text{ mole} \cdot \text{m}^{-2}$). The measurements were carried out using a Tacussel bipotentiostat, Type BIPAD.

The KOH solution (prepared with p.a. quality KOH and doubly distilled water) was purified by preelectrolysis, made oxygen-free, and kept in Ar atmosphere. Hydrogen peroxide was added¹ and anodic and cathodic limiting currents at the ring were measured while the disk current was zero. To avoid poisoning of the ring by the stabilizer from the H_2O_2 solution used, the currents were measured by cyclic voltammetry with scan rates of 100-500 $\text{mV} \cdot \text{sec}^{-1}$. The rest potential at the disk was measured to be 889 mV *vs.* a reversible hydrogen electrode in the same solution and was independent of the rotation frequency. Therefore it was possible to obtain the H_2O_2 concentration from a $I_{R,\text{lim}}^a$ *vs.* $\sqrt{\omega}$ -plot. The slope of this plot gave $c_2^s = 5.3 \text{ mM}$, which value was verified by titration with KMnO_4 . The results, plotted as $I_{R,\text{lim}}/2N_o A F c_2^s$ *vs.* $\gamma_2 \sqrt{\omega}$, are given in Fig. 3. The

¹ Brocacef, 30% v/w, Ph. Eur.

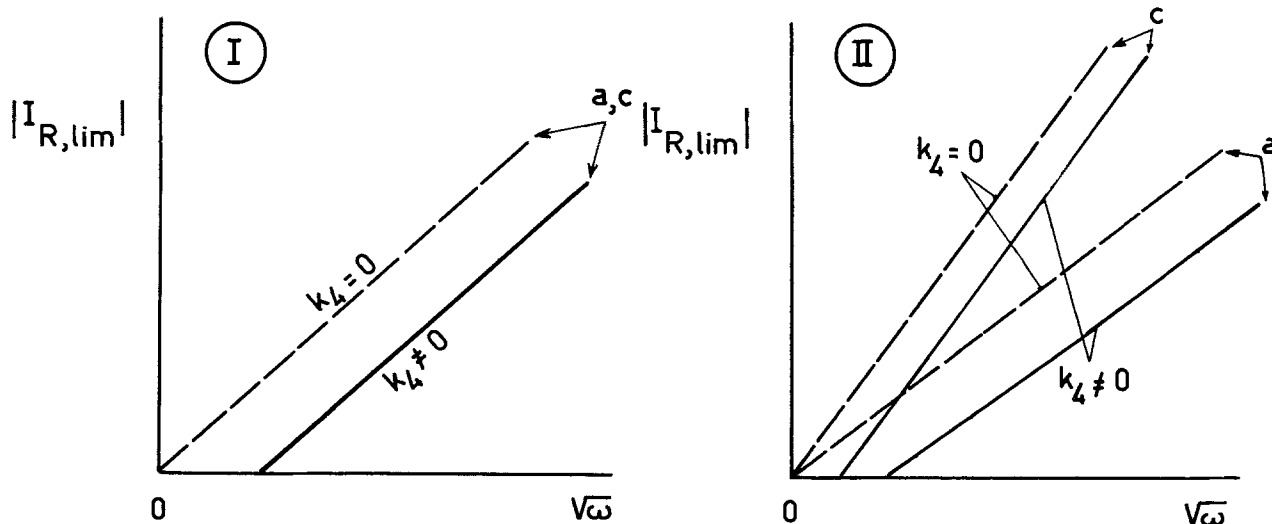


Fig. 2. Limiting cases of Eq. [8] and [9] (arbitrary units). I: $K \ll 1$; II: $K \gg 1$; a = anodic; c = cathodic limiting current; - - - for $k_4 = 0$; — for $k_4 \neq 0$.

slope of the anodic branch is calculated to be 1.98 ± 0.06 , in very good agreement with the theoretical value of

$$\frac{\beta^{2/3}}{N_0} = 1.978$$

From the slope of the cathodic branch (2.89 ± 0.07), the value of $K = 10.1$ can be calculated. This means that H_2O_2 is, electrochemically approximately five times more reactive at a gold electrode than O_2 .

The intercepts of the anodic and cathodic branches are, respectively, $-0.12 \times 10^{-4} \text{ msec}^{-1}$ and $-0.17 \times 10^{-4} \text{ msec}^{-1}$. This gives, by application of Eq. [8] and [9], $k_4 = (1.6 \pm 0.3) \times 10^{-4} \text{ msec}^{-1}$. Calculation according to Eq. [10] gives $k_4 = (1.6 \pm 0.2) \times 10^{-4} \text{ msec}^{-1}$.

Conclusion

As shown in the introduction, there are two nodal points in the scheme of reactions for O_2 reduction where a distinction is to be made between possible paths. The first is where oxygen can give either H_2O or H_2O_2 . Here, RRDE experiments in O_2 -containing solutions enable us to make the distinction. The second is where hydrogen peroxide can react either electrochemically or chemically. The method proposed here makes it possible to determine whether or not H_2O_2 decomposes chemically. In those cases where it may be assumed that k_4 does not depend on the disk electrode potential, it is even possible to calculate the magnitude of k_4 . This assumption is valid as long as the catalytic properties of the electrode surface for the decomposition of H_2O_2 do not change significantly when the electrode potential is changed from the rest potential.

Furthermore, the method described here is simpler than that given recently by Appleby and Savy (10). They use an RRDE with a pyrolytic graphite ring, at which H_2O_2 is stable, to find k_4 . This means that they need two different RRDE's, one to find k_1 , k_2^f , k_2^b , and k_3 in oxygen-containing solutions and another one for use in solutions containing H_2O_2 to find k_4 .

Acknowledgment

This work has been carried out with financial support from the Netherlands Organization for the Advancement of Pure Research (ZWO).

Manuscript received Nov. 7, 1979.

Any discussion of this paper will appear in a Discussion Section to be published in the June 1981 JOURNAL. All discussions for the June 1981 Discussion Section should be submitted by Feb. 1, 1981.

Publication costs of this article were assisted by the University of Technology.

LIST OF SYMBOLS

A	disk area (m^2)
c^0	concentration near disk surface (mole m^{-3} = mM)
c^s	concentration in solution (mole m^{-3} = mM)
D	diffusion coefficient ($\text{m}^2 \text{ sec}^{-1}$)
E_D	disk potential (V)
F	Faraday constant
I_D	disk current (A)
$I_{D,\text{lim}}^{\text{H}_2\text{O}}$	limiting disk current for reaction $\text{O}_2 \rightarrow \text{H}_2\text{O}$ (A)
$I_{D,\text{lim}}^{\text{H}_2\text{O}_2}$	limiting disk current for reaction $\text{H}_2\text{O}_2 \rightarrow \text{O}_2$ or $\text{H}_2\text{O}_2 \rightarrow \text{H}_2\text{O}$ (A)
I_R	ring current
$I_{R,\text{lim}}$	limiting current (A)
k	reaction rate constant (see Fig. 1) (msec^{-1})
K	pseudo constant, defined in formula [9]
N_0	collection efficiency of RRDE
β	geometric factor of RRDE
γ	$0.62 D^{2/3} \nu^{-1/6}$ ($\text{msec}^{-1/2}$)
ν	kinematic viscosity ($\text{m}^2 \text{ sec}^{-1}$)
ω	angular rotation frequency of RRDE (sec^{-1})

Superscripts

a	anodic
c	cathodic

Subscripts

1	O_2
2	H_2O_2
r	refers to rest potential

REFERENCES

- V. S. Bagotskii *et al.*, *Sov. J. Electrochem.*, **4**, 1129 (1968); *ibid.*, **5**, 1158 (1969).
- A. Damjanovic, M. A. Genshaw, and J. O'M Bockris, *J. Chem. Phys.*, **45**, 4057 (1966).
- J. D. E. McIntyre, *J. Phys. Chem.*, **73**, 411 (1969).
- M. R. Tarasevich, *Sov. J. Electrochem.*, **4**, 182 (1967); *ibid.*, **6**, 1468 (1970).
- Yu. V. Pleskov and V. Yu. Filinovskii, "The Rotating Disc Electrode," Consultants Bureau, New York/London (1976).
- H. S. Wroblowa, Yen-Chi-Pan, and G. Razumney, *J. Electroanal. Chem. Interfacial Electrochem.*, **69**, 195 (1976).
- W. J. Albery and M. L. Hitchman, "Ring Disc Electrodes," Clarendon Press, Oxford (1971).
- M. R. Tarasevich and K. A. Radyushkina, *Sov. J. Electrochem.*, **6**, 370 (1970).
- J. F. van der Plas and E. Barendrecht, *Rec. Trav. Chim. Pays Bas*, **96**, 133 (1977).
- A. J. Appleby and M. Savy, *J. Electroanal. Chem. Interfacial Electrochem.*, **92**, 15 (1978).