

**NEW PROCEDURE FOR LINEAR SWEEP VOLTAMMETRIC
DETERMINATION OF CATALYTIC REACTION RATE CONSTANT.
OXIDATION OF SOME ALIPHATIC ALCOHOLS WITH
ELECTROLYTICALLY GENERATED Os(VIII)**

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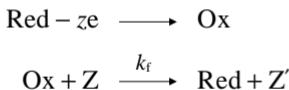
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Oxidation rate of methanol, ethanol and 2-propanol by Os(VIII) in 1 M KOH was determined by evaluating anodic voltammograms of Os(VI) in the presence of the aliphatic alcohols. The proposed method is based on the evaluation of the change of voltammogram shape by catalytic process and on the assumption of its approximation by fractionally integrated voltammograms. This assumption has been confirmed empirically for k_f/a in the interval of $<0.04, 1>$. The rate constants from this interval could be determined with sufficient accuracy. The method is suitable for evaluation of reaction rates slow and moderately fast catalytic reactions. It was compared with other evaluation methods from the literature.

Catalytic currents were frequently used for measurement of reaction rates of electrochemically generated reactants with electroinactive species in solution. Polarography and cathodic generation of reductant species dominate in this application¹. An application of anodic linear sweep voltammetry is less frequent because of some problems in evaluating the results². In contrast with polarography, catalytic reaction leads to a substantial change of voltammogram shape in addition to differences in limiting current value. Gradual change from a diffusion controlled non-symmetrical peak to a wave-formed voltammogram corresponds to the gradual increase of catalytic reaction rate². This change, which is dominant for low rates of catalytic reactions may cause some problems in evaluation of voltammograms.

In our previous study³ we have developed a method for determination of catalytic reaction rate constant based on the fractional integration of linear sweep voltammograms. The procedure was tested with good results using catalytic reaction of Ti^{3+} with NH_2OH .

The present paper reports our study of anodic catalytic current of the type:



where Red is Os(VI), Ox is Os(VIII), number of electrons $z = 2$, Z is the alcohol: methanol, ethanol and 2-propanol and Z' is the corresponding product of chemical oxidation.

EXPERIMENTAL

All chemicals were of analytical grade purity. The stock solution of osmium tetroxide was prepared by dissolving 1 g of OsO₄ (Johnson Matthey Chemicals Ltd., U.S.A.) in 500 ml of 0.1 M H₂SO₄. The amount of 50 ml of this solution was mixed with 2.2 M KOH solution to the total volume of 100 ml. Before every measurement, Os(VIII) was reduced coulometrically in the alkaline solution to Os(VI) at -0.2 V vs Ag/AgCl on a Pt-Wikler's electrode. The solution of Os(VI) in KOH is not stable at a room temperature and its decomposition can be easily indicated by the appearance of a light brown color of Os(VIII). At temperatures below 0 °C the solution is stable for more than a week. Aliquots from this solution were taken for daily use and their concentrations were determined coulometrically.

The voltammetry was performed by means of the EG&G PAR Model 273A potentiostat/galvanostat controlled by the computer. Three-electrode arrangement was used with an SCE reference electrode and a platinum auxiliary electrode. The working electrode was cylindrical shape with an area of 90 mm². The electrode has been activated by the cyclic voltammetry with the scan rate of 100 V s⁻¹ in the potential range from +0.2 to -0.8 V vs SCE for 10 min in 1 M H₂SO₄. Between two successive cycles the electrode was polarized for 1 s to -0.8 V vs SCE. This procedure was repeated every time before the measurement was started.

Alkaline solution of Os(VI), stored at 0 °C, was heated to 20 °C. Aliquot volume, 10 ml, was pipetted to the electrolytic cell. After deaeration the voltammogram was recorded both in absence and in presence of catalytic species. The scan rate for methanol was 10 mV s⁻¹, for ethanol 25 mV s⁻¹ and for 2-propanol 200 mV s⁻¹. Scan range was from -0.1 to +0.5 V vs SCE. The temperature of the electrochemical cell was maintained at 20 ± 1 °C.

RESULTS AND DISCUSSION

Catalytic Reaction Rate Evaluation

The evaluation procedure was developed in attempt to improve the linear sweep voltammetric method for quantitative analysis using a computer elimination of voltammogram deformation caused by a catalytic reaction³. The idea was to eliminate the influence of regeneration of electroactive catalytic species, which could make the quantitative analysis impossible. Experimentally, the influence of product regeneration can never be excluded due to the presence of other reactant in a real sample.

The elimination of an influence of catalytic reaction on linear sweep voltammogram is based on symmetrization transformation by optimum order fractional differentiation.

Semidifferentiation often applied for symmetrization of diffusion-controlled voltammograms⁴⁻⁷ is a special case of this more general procedure. To get the symmetrical peak for a voltammogram influenced by a slow catalytic process, its fractional differentiation was proposed, the order of which was in the interval <1,0.5>.

The optimum order of the fractional differentiation (symmetrization) q depends on the rate constant of the catalytic reaction and so does the height of the resulting symmetrized peak. The optimum order should be determined for every individual voltammogram on the basis of its shape analysis. This is done by a computer routine called ITER (ref.⁸) which in addition enables also the execution of fractional differentiation itself.

“Working curves” – the dependences of symmetrical peak heights or corresponding optimum differentiation order vs k'_f/a – necessary for evaluation of catalytic reaction rate were constructed using simulated voltammograms. Simulation of linear sweep voltammograms of reversible charge transfer, coupled with an irreversible catalytic reaction for different k'_f/a (k'_f is the catalytic reaction rate constant, $a = zFv/RT$, v is the scan rate, z is the number of exchanged electrons while F , R and T have their usual meanings), was done using a computer routine CONDESIM supplied by EG&G PAR (Princeton, NJ, U.S.A.).

Simulated voltammograms for k'_f/a ranging between 0 and 1 were symmetrized using routine ITER. The heights of the resulting symmetrical peaks grow with increasing k'_f/a as shown in Fig. 1, curve 2. The slope of curve 2 is larger than the slope of the dependence of original non-symmetrical peak heights versus k'_f/a (Fig. 1, curve 1). The symmetrized signals are thus more sensitive to the catalytic process. It can also be seen in Fig. 1, curve 3 that the higher is the rate constant, the higher is the optimum order of symmetrization differentiation q . The dependence can be sufficiently approximated by the polynomial function of fourth order

$$q = 0.51 + 1.99(k'_f/a) - 3.66(k'_f/a)^2 + 3.66(k'_f/a)^3 - 1.19(k'_f/a)^4.$$

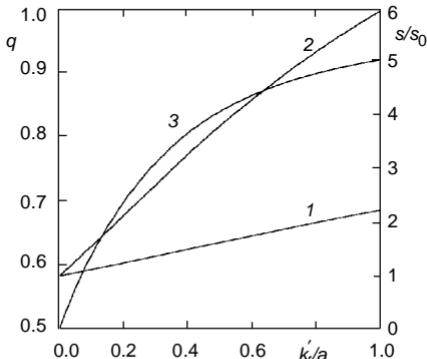


FIG. 1
Ratio of catalytic (s) to diffusion (s_0) controlled signals (curves 1, 2) and optimum peak differentiation order versus k'_f/a dependences (curve 3). Curve 1 is for original linear sweep voltammogram, 2 for symmetrized peak, k'_f is the catalytic reaction rate constant multiplied by catalyzed species concentration, $a = zFv/RT$, v is the sweep rate and z is the number of exchanged electrons

Oxidation of Some Aliphatic Alcohols with Electrochemically Generated Os(VIII)

Os(VIII) was electrochemically generated from Os(VI) in the solution. The peak potential of Os(VI) oxidation was 0.20 V and the peak potential of Os(VIII) reduction was 0.12 V vs SCE in 1 M KOH.

Studied organic species – aliphatic alcohols are not anodically active in the potential range of Os(VI) electrode oxidation. In agreement with result of Kalvoda and co-workers¹⁰ we have found that the rate of oxidation of aliphatic alcohol by Os(VIII) depends on OH^- concentration. Since it was not our aim to study reaction mechanism or its rate dependence on the length of aliphatic chain, we have limited our experiments to 1 M KOH solution of methanol, ethanol and 2-propanol. Voltammograms of Os(VI) in the presence of different concentrations of alcohols were evaluated to obtain catalytic reaction rate constants.

The correct procedure in a linear sweep voltammetry is fitting the shape of the voltammogram to calculated curves², which is rather less convenient in practical application. Another possibility to determine the rate constant is to evaluate the ratio between catalytic and diffusion-controlled peak heights. This way is not applicable for the lower values of rate constants because of the low slope of the ratio dependence on k'_f/a (Fig. 1, curve 1). As it is shown in Fig. 1, the dependence of the corresponding

TABLE I

Rate constants of catalytic reactions for aliphatic alcohols obtained by evaluating optimum order of differentiation q . Concentration of Os(VI) was $3.93 \cdot 10^{-3}$ mol dm^{-3} and scan rate for MeOH $v = 10$ mV s^{-1} , for EtOH $v = 25$ mV s^{-1} and for 2-PrOH $v = 200$ mV s^{-1}

c_Z mol dm^{-3}	MeOH		EtOH		2-PrOH	
	q	$10^2 k'_f/c_Z$ $\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$	q	k'_f/c_Z $\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$	q	k'_f/c_Z $\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$
0.10	–	–	–	–	(0.53)?	(1.35)?
0.20	(0.52)?	(3.61)?	0.56	0.248	0.54	1.36
0.50	0.56	3.48	0.57	0.237	0.59	1.33
0.91	0.59	3.78	0.68	0.232	0.64	1.34
1.67	0.64	3.65	0.79	0.238	0.73	1.37
2.31	0.69	3.71	0.84	0.219	0.78	1.31
2.86	0.71	3.40	0.88	0.224	0.82	1.33
3.33	0.72	3.20	(0.92)?	(0.231)?	0.86	1.36
3.75	0.75	3.30	–	–	0.88	1.34

ratios for symmetrized peaks is much steeper. The rate constant values determined by means of curve 2 are, therefore, more accurate. The dependence of optimum q versus k_f'/a (Fig. 1, curve 3) offers still further possibility to evaluate the rate constant of a slow or moderately fast catalytic reaction. The last mentioned possibility was applied in this paper and its results were summarized in Table I.

The proposed method of catalytic rate constant evaluation was compared with methods described in the literature. The comparison is shown in Figs 2, 3 and 4 for methanol (MeOH), ethanol (EtOH) and for 2-propanol (iPrOH), respectively. Values of k_f'/c_Z obtained by our method (curves 1) evidently do not depend on concentration of alcohol c_Z . This is in an agreement with the expectation, that the chemical reaction between Os(VIII) and alcohols appears to be first order with respect to the concentration of alcohol⁹. As it can be seen from Figs 2–4, curves 2, the independence of k_f'/c_Z on c_Z is not fulfilled if a method based on Table XII, or Fig. 14 from ref.² was used to reevaluate the results of Kalvoda and co-workers⁹. The k_f'/c_Z values at curves 2 do not look like results scattered around the mean value as it is in the case of curves 1. An explicit trend can be followed especially for lower c_Z . On the other hand a

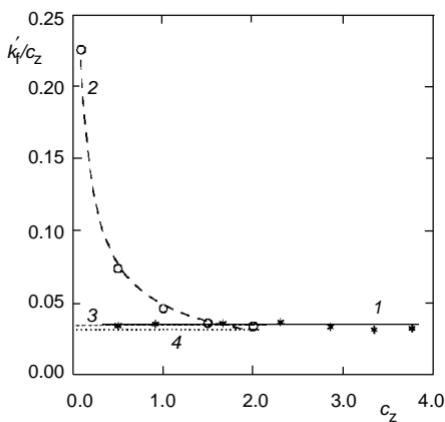


FIG. 2

Dependences of k_f'/c_Z ($\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$) on concentration of methanol c_Z (mol dm^{-3}): 1 Results obtained by evaluation of optimum order fractional differentiation (—), $v = 10 \text{ mV s}^{-1}$; 2 results from ref.⁹ reevaluated according to Table XII or Fig. 14 from ref.² (—), $v = 2.77 \text{ mV s}^{-1}$; 3 k_f'/c_Z value obtained by procedure described in ref.⁹ (---), $v = 2.77 \text{ mV s}^{-1}$, temperature 20°C ; 4 k_f'/c_Z value obtained from coulometric measurements – steady state current¹⁰ (....), temperature 22°C

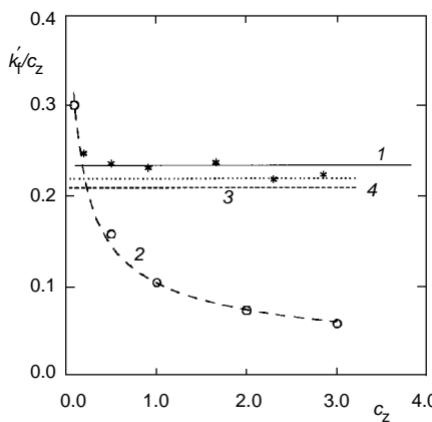


FIG. 3

Dependences of k_f'/c_Z ($\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$) on concentration of ethanol c_Z (mol dm^{-3}): 1 Results obtained by evaluation of optimum order fractional differentiation (—), $v = 25 \text{ mV s}^{-1}$; 2 results from ref.⁹ reevaluated according to Table XII or Fig. 14 from ref.² (—), $v = 2.77 \text{ mV s}^{-1}$; 3 k_f'/c_Z value obtained by procedure described in ref.⁹ (---), $v = 2.77 \text{ mV s}^{-1}$, temperature 20°C ; 4 k_f'/c_Z value obtained from coulometric measurements – steady state current¹⁰ (....), temperature 22°C

surprisingly good agreement of our results ($0.035 \pm 0.002 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ for methanol, $0.233 \pm 0.011 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ for ethanol and $1.34 \pm 0.02 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ for 2-propanol; 20 °C, 1 M KOH) with those obtained by the method published in ref.⁹ was found. At the same time the results are in a good agreement with those obtained from coulometric measurements based on the evaluation of steady state currents¹⁰.

A possible reason for changes of k'_f/c_Z with c_Z can be very low scan rate ($2.77 \cdot 10^{-3} \text{ V s}^{-1}$) applied in voltammetric measurements in ref.⁹. The time scale of the experiment in this case is rather long (70 – 100 s) and the influence of convection transport can not be excluded. The method proposed in this paper is based on the evaluation of change of linear sweep voltammogram and it is much more sensitive to the influence of catalytic reaction (Fig. 1) allowing to increase the scan rate and to avoid the influence of uncontrolled convection. Scan rates higher than 10 mV s^{-1} are commonly used in linear sweep voltammetry.

From what it has been said, it is evident that the method is actually based on the assumption that the shapes of catalytically influenced voltammograms can be approximated by fractionally integrated voltammograms. The assumption has been confirmed empirically only for $k'_f/a < 1$. On the other hand the value of k'_f/a should not be lower than 0.04 to get the optimum q value (0.53) sufficiently differing from 0.5 which corresponds to the diffusion limited current. The application of the method is thus limited to the q interval $<0.53, 0.9>$. The optimum order q is produced by routine ITER for each particular case, enabling an easy consideration of applicability of the method. The interval of $k'_f/a < 0.04, 1>$ indicates that the proposed method of catalytic reaction rate evaluation can be used mainly for slow and moderately fast catalytic reactions.

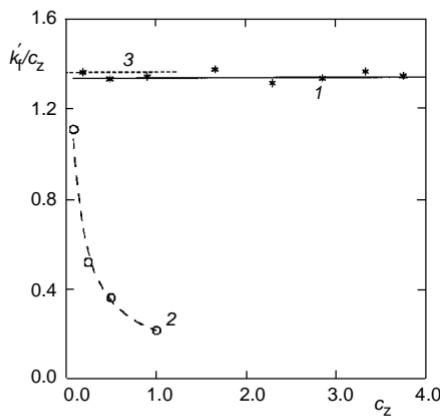


FIG. 4
Dependences of k'_f/c_Z ($\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$) on concentration of 2-propanol c_Z (mol dm^{-3}): 1 Results obtained by evaluation of optimum order fractional differentiation (—), $v = 200 \text{ mV s}^{-1}$; 2 results from ref.⁹ reevaluated according to Table XII or Fig. 14 from ref.² (— —), $v = 2.7 \text{ mV s}^{-1}$; 3 k'_f/c_Z value obtained by procedure described in ref.⁹ (---), $v = 2.77 \text{ mV s}^{-1}$, temperature 20 °C

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