OXIDATION SCHEME OF SYMMETRICALLY DISULPHONATED NAPHTHIDINES WITH CERIUM(IV) SULPHATE*

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The author derived theoretical dependences of preasymptotic slopes of the currentless $E-t$ curves (potential of an indicator redox electrode against time) on the number of equivalents, n, of added oxidation agent, assuming a reaction scheme of two consecutive concurrent second-order reactions involving the formation of intermediate products (a side reaction of the starting compound with the final oxidation product leading to an adduct, which undergoes consecutive bimolecular oxidations leading again to the final product). These dependences enable to determine the type of the relatively stable intermediate products and the ratios of the rate constants. The theory was applied to the oxidation of four symmetrically disulphonated naphthidines with cerium(IV) sulphate in aqueous sulphuric acid and the results were substantiated spectrophotometrically.

The oxidation of 1-aminonaphthalene-X-sulphonic acids with cerium sulphate in aqueous sulphuric acid was already studied by us[1,2] for X = 8 and later[3] for X = 2, 6, and 7. The intermediate products of this reaction are naphthidine derivatives, which are symmetrically disubstituted with sulpho groups in positions 7,7' (compound *I*), 6,6' (compound *II*), 5,5' (compound *III*), and 3,3' (compound *IV*); their further oxidation plays a substantial role in the overall reaction mechanism. Therefore, we studied specially the oxidation of compounds *I*–*IV* under the same conditions. The investigation of these relatively complicated and rapid reactions is rendered difficult in view of a limited choice of suitable analytical methods; we used the method of currentless $E-t$ curves and compared the results with spectrophotometric measurements of the red reaction mixtures in the course of the oxidation.
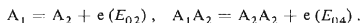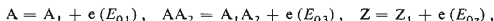
THEORETICAL

We shall consider the following reaction scheme involving two consecutive concurrent reactions and a parallel formation of intermediate products:
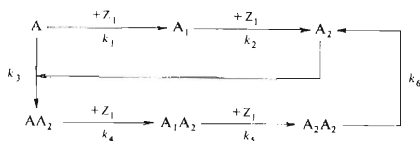
Here the subscripts of the reaction components denote their formal oxidation state, k_1 through k_6 are rate constants of the individual reaction steps. This complicated reaction scheme can be studied by analysing the dependence of the preasymptotic slope, S, of the E-t curves on the molar ratio of the starting compounds, $n = z/b$ (i.e., the ratio of the starting concentrations of compounds Z_1 and A) in a similar way as in references[4,5].

The reacting mixture contains the following independent redox systems with the standard redox potentials E_{0i}:

$$A = A_1 + e \, (E_{01}) , \quad AA_2 = A_1A_2 + e \, (E_{03}) , \quad Z = Z_1 + e \, (E_{0z}) ,$$

$$A_1 = A_2 + e \, (E_{02}) , \quad A_1A_2 = A_2A_2 + e \, (E_{04}) .$$

The general equation of the E-t curve[6] takes by neglecting the electrode reaction the form

$$\frac{\sum \mathscr{R}_i P_{\alpha_1}(A_i) + \mathscr{R}_z P_{\alpha z}(Z_1)}{\sum \mathscr{R}_i P_{1-\alpha_1}(A_i) + \mathscr{R}_z P_{1-\alpha z}(Z)} = 1 , \tag{1}$$

where the dimensionless relative concentrations of the reactants are expressed as $(A_i) = [A_i]/b$, $(Z_i) = [Z_i]/b$ (the brackets refer to the actual concentrations of the reactants).

Further we shall make the following simplifying assumptions: *1*) The reaction components A_1 and A_2A_2 are during the reaction in a stationary state and their concentration is considered negligible. The compound A_1 is an unstable one-electron oxidation product (a free radical), the adduct A_2A_2 decomposes rapidly to $2A_2$.

2) The standard redox potential of the reaction $Z = Z_1 + e$ (of the oxidant), E_{0z}, is much higher than that of the other redox systems present in the mixture. Therefore, only the term $\mathscr{R}_z P_{\alpha z}(Z_1)$ in Eq. (*1*) plays a role (owing to a high value of $P_{\alpha z}$), whereas the terms $\mathscr{R}_1 P_{1-\alpha_1}(A_1)$ and $\mathscr{R}_z P_{1-\alpha z}(Z)$ in the denominator can be neglected because of negligible values of (A_1) and $P_{1-\alpha z}$.

3) Of the remaining three terms in the denominator, Eq. (*1*), only one need be considered, whereby this equation simplifies to

$$\frac{\mathscr{R}_z P_{\alpha z}(Z_1)}{\mathscr{R}_i P_{1-\alpha_1}(A_i)} = \frac{\mathscr{R}_z \exp\left[-(E - E_{0z}) \, \alpha_z F/RT\right](Z_1)}{\mathscr{R}_i \exp\left[(E - E_{0i}) \, (1 - \alpha_i) \, F/RT\right](A_i)} = 1 . \tag{2}$$

Here (A_i) stands for (A), (AA_2) or (A_1A_2), and E denotes potential of the indicator electrode in the mixture of the reacting redox systems. The dependence of E on the dimensionless time $\tau = bk_1t$ can be expressed as

$$(dE/d\tau) \, y_{iz} = d \ln (Z_1)/d\tau - d \ln (A_i)/d\tau . \tag{3}$$

The quantity $y_{i\alpha} = (1 - \alpha_i + \alpha_Z)\, F/RT$ involves the transfer coefficients α_i and α_Z for the corresponding redox systems. The terms $d\ln(Z_1)/d\tau$ and $d\ln(A_i)/d\tau$ can be easily obtained from differential kinetic equations for Z_1 and A_i valid for the above-mentioned reaction scheme and expressed in dimensionless concentrations and parameters $\xi = k_3/k_1$, $\omega = k_4/k_1$, $\sigma = k_5/k_1$:

$$-d(A)/d\tau = (A)(Z_1) + \xi(A)(A_2),\qquad(4)$$

$$d(AA_2)/d\tau = \xi(A)(A_2) - \omega(AA_2)(Z_1),\qquad(5)$$

$$d(A_1A_2)/d\tau = \omega(AA_2)(Z_1) - \sigma(A_1A_2)(Z_1),\qquad(6)$$

$$d(Z_1)/d\tau = 2(A)(Z_1) + \omega(AA_2)(Z_1) + \sigma(A_1A_2)(Z_1),\qquad(7)$$

$$d(A_2)/d\tau = (A)(Z_1) - \xi(A)(A_2) + 2\sigma(A_1A_2)(Z_1).\qquad(8)$$

The relative concentrations of the reactants fulfil the conditions

$$(A) + (A_2) + 2(AA_2) + 2(A_1A_2) = 1,\qquad(9a)$$

$$(Z_1) + (Z) = n,\qquad(9b)$$

and the condition for the number of transferred electrons is

$$2(A_2) + 2(AA_2) + 3(A_1A_2) = (Z).\qquad(9c)$$

Our aim is to find the dependence $S = (dE/d\tau)\, y_{iz} - n$ for the preasymptotic portion of the E–t curves, where the reaction is practically finished. Since the proportionality coefficient y_{iz} is unknown, the quantity S is determined as $(dE/d\tau)_n/(dE/d\tau)_{n=0}$, i.e., it is normed by the coordinate of the starting point $S = 2$, $n = 0$.

In the final reaction stage we have (in addition to the compound Z) in the interval $n(0; 1)$ to deal only with compounds A and AA_2 in concentrations $(A)_\infty = 1 - n$ and $(AA_2)_\infty = n/2$. For $n(1; 1.5)$ we have $(A)_\infty = 0$ $(AA_2)_\infty = (3 - 2n)/2$ and $(A_1A_2)_\infty = n - 1$; for $n(1.5; 2)$ we have $(A)_\infty = (AA_2)_\infty = 0$ $(A_1A_2)_\infty = 2 - n$, $(A_2)_\infty = 2n - 3$; and for $n > 2$ we have $(A_2)_\infty = 1$, $(Z_1)_\infty = n - 2$. By substituting the terms $d\ln(Z_1)/d\tau$ and $d\ln(A_i)/d\tau$, calculated from Eqs (4)–(8), into Eq. (3), considering the given conditions for different intervals of n values and rearranging we obtain the theoretical S–n dependences for the preasymptotic portions of the E–t curves, which are given in Table I. These are shown graphically in Fig. 1. In the case where the term with (A) in the denominator of Eq. (2) becomes important, the dependence in the interval $n(0; 3)$ consists of four linear portions, whereas in the cases where (AA_2) or (A_1A_2) become important, it consists of three linear portions. The points where the linear dependence is broken characterize not only the type of intermediate reaction products (the break at $n = 1$ corresponds to the formation of a one-electron product AA_2, that at $n = 1.5$ to A_1A_2 with a one and a half-electron oxidation stage, that at $n = 2$ to a two-electron oxidation to A_2), but also the ratios of the corresponding rate constants ω, σ, and ξ.

TABLE I

Reaction Scheme: Equations for $S–n$ Dependences in Different Intervals of n Values

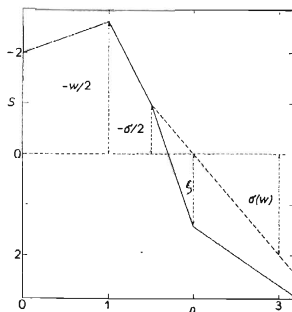| Interval n	Important term in denominator of Eq. (2)	Function $S(n)$
0; 1	A or A_1A_2 or AA_2	$S = n(2 - \omega/2) - 2$
1; 1·5	A or A_1A_2 or AA_2	$S = n(\omega - \sigma) + \sigma + 1·5\omega$
1·5; 2	A	$S = n(\sigma - 2\xi) - (2\sigma + 3\xi)$
	AA_2 or A_1A_2	$S = \sigma(n - 2)$
2	A	$S = n - 2 + \xi$
	AA_2	$S = \omega(n - 2)$
	A_1A_2	$S = \sigma(n - 2)$

FIG. 1

Illustrative Dependences of S on n for Reaction Scheme

Beginning from $n = 1·5$, the solid line refers to the case where the term (A) in the denominator of (2) plays a role, the dashed line refers to the case where the terms with (AA_2) or (A_1A_2) become important. The conditions $\omega < 4$, $\sigma > \omega$ apply.
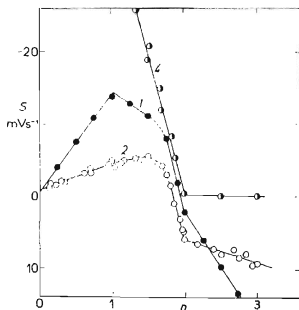

FIG. 2

Dependence of dE/dt on n for Compounds I (1), II (2), and IV (4)

Numbers of the curves refer to the compounds. Compounds I and II were oxidised at $H_0 = -3$, compound IV at $H_0 = -4$; 20°C.

EXPERIMENTAL

Apparatus

The $E-t$ curves were recorded by using the experimental equipment described earlier[7] without an inert atmosphere in view of the relative stability of the strongly acidic solutions of compounds $I-IV$. The indicator electrode was smooth platinum; a saturated Hg/Hg_2SO_4 electrode served as reference.

The dependences of the absorbance of the reaction mixture, a, at a suitable wave length on the time, t, with n as parameter were measured on a spectrograph of the type Specord UV-VIS (Zeiss, Jena, GDR) with a built-in mixing and tempering adapter[8] enabling a perfect mixing of the reaction components within a second and tempering in the interval from -20 to $+60°C$ with an accuracy to $\pm 0.1°C$ in 2 cm thick glass cuvettes holding 30 ml of solution. With compound IV, which was extremely rapidly oxidised, a stop-flow apparatus of the type D 110 (Durrum Instrument Corp., USA) was used, in which the time of mixing was about 10^{-3} s at a cuvette thickness of 2 cm. The measurement was carried out at the maximum absorbance of the red oxidation mixture, i.e., at 525 nm with compounds I and II, at 510 nm with compound III, and at 570 nm with IV. The dependence of the maximum absorbance, a_∞, at the final stage of the reaction on n was obtained from a set of $a-t$ curves by plotting the values of a for sufficiently large values of t, where the absorbance was constant, against n.

Chemicals

The compounds $I-IV$ were prepared by the method described by us[2] except that the diazonium salt was reduced to the azo compound by a saturated aqueous solution of Na_2SO_3 in the medium of sodium acetate (16 g of the acetate in 75 cm^3 of water). Thus, the yields were somewhat higher. A standard solution of the starting compound was prepared by weighing, suspending in redistilled water, adding pyridine dropwise (reagent grade) to dissolution and making up to the mark with water. The maximum concentration of the standard solution was 0·01 mol/dm^3. Since it was sensitive against oxidation (it turned brown), it was stored in the dark and solutions older than one week were discarded. The factor of the standard solution was determined by potentiometric titration with a standard solution of KOH with an antimony-saturated calomel electrode couple. The starting reaction mixture containing $10^{-4}-10^{-5}$ mol/dm^3 reactants was prepared by diluting the stock solution of the pyridinium salt with the given reaction medium. A standard solution of 0·01 mol/dm^3 $Ce(SO_4)_2$ was prepared from $Ce(SO_4)_2.4 H_2O$ of reagent grade (Merck, GFR) by dissolving in a diluted sulphuric acid whose pH was the same as that of the reaction medium. The factor of this solution was determined potentiometrically with a standard solution of $Fe(NH_4)_2(SO_4)_2$. The reaction medium was aqueous sulphuric acid whose acidity was defined by the Hammett acidity function H_0.

RESULTS AND DISCUSSION

The oxidation of compounds $I-IV$ was studied at room temperature mainly in strongly acidic media (H_0 from -3 to -4), where the red products were relatively most stable (about 10 min at 20°C). At a lower acidity, these products decompose more rapidly to practically colourless compounds and the reaction rate increases considerably.

COMPOUNDS *I* AND *II*

E-t Curves

By plotting the potential of the indicator electrode, E_∞, at the final stage of the reaction (read from the set of *E-t* curves with *n* as parameter) against *n*, we obtain a curve with a potential jump for $n = 2$, an evidence for a two-electron oxidation. Since a trimolecular reaction $(A + 2Z_1 \rightarrow \ldots)$ is improbable, a consecutive oxidation $A \rightarrow A_1 \rightarrow A_2$ must form the base of the oxidation scheme. The form of the $dE/dt-n$ curves (Fig. 2, curves *1* and *2*) with breaks for $n = 1$, 1·5 and 2 suggests that the consecutive oxidation is accompanied by the formation of intermediate products, *e.g.*, according to the reaction scheme given in the theoretical part by the compounds AA_2, A_1A_2. Then, of course, the ordinates of the mentioned breaks, eventually of the point for $n = 3$ must correspond to the ratios of the rate constants ω, σ, and ξ on the *S-n* curve (Fig. 1). In this way we found the values of these ratios for the oxidation of compounds *I* and *II* and these are given in Table II.

Spectrophotometry

The ratio of actual absorbances measured in a reaction mixture in such a region of the visible spectrum where neither the starting compounds A and Z_1 nor the product Z absorb fulfils the equation

$$a(\lambda_1, t)/a(\lambda_2, t) = \text{const.} \qquad (10)$$

This requires the validity of the relation $\varepsilon_i(\lambda) = k_i \varepsilon_{A_2}(\lambda)$ with k_i independent of λ, where ε_i denotes molar decadic absorption coefficients of all oxidation products of the compound A in the reaction mixture.

TABLE II]

Ratios of Rate Constants ω, σ, and ξ for Oxidation of Compounds *I* and *II* at 20°C with $Ce(SO_4)_2$ in Aqueous H_2SO_4 Obtained by Analysis of *S-n* Curves

Acidity of the medium is given by the Hammett acidity function H_0.

Compound	H_0	ω	σ	ξ
I	—3	96	74	8
II	—4	15	18	6
	—3	23·2	27·4	15
	—2	15	16	18·6
	—1	14	12·8	5

Dependence of a_∞ on n

This dependence increases linearly with n up to $n = 2$ attaining a constant value for $n > 2$. The break at $n = 2$ is an evidence for a two-electron oxidation. We assume that the reaction mixture contains the species A, A_2, AA_2, A_1A_2, Z_1, and Z, of which A, Z_1 and Z do not absorb light in the given region of wave lengths. Based on the final concentrations $(A_iA_2)_\infty$, the total absorbancy of the final reaction mixture is given by the equations

$$n(0; 1): \qquad a_\infty = \tfrac{1}{2}\varkappa_{02}n \qquad\qquad (11a)$$

$$n(1; 1\cdot5): \qquad a_\infty = \varkappa_{02}(3 - 2n)/2 + \varkappa_{12}(n - 1) \qquad (11b)$$

$$n(1\cdot5; 2): \qquad a_\infty = \varkappa_{12}(2 - n) + \varkappa_2(2n - 3) \qquad (11c)$$

$$n > 2: \qquad a_\infty = \varkappa_2 , \qquad\qquad (11d)$$

where $\varkappa_{i2} = \varepsilon_{i2}\,db$ and d is the thickness of the cuvette. The mentioned experimental dependence can be expressed as $a_\infty = \text{const.}\ n$ for $n \leqq 2$ and $a_\infty = 2.\ \text{const.}$ for $n > 2$; this can be brought into agreement with the theory only if $\varepsilon_{02} \equiv \varepsilon_2$ and $\varepsilon_{12} = \tfrac{3}{2}\varepsilon_2$. This in turn implies that only the species A_2 is responsible for the absorption of light in AA_2, whereas the absorbancy of A_1A_2 is due also to the species A_1, which has a radical character. It can be shown by substitution into $(11b,c)$ that the linearity of the a_∞–n dependence is preserved also in the interval $n(1; 2)$ with a maximum relative error of $\pm 13\%$ for $n = 1\cdot5$, if the value of ε_{12} lies in the interval from $1\cdot4\varepsilon_2$ to $1\cdot7\varepsilon_2$.

Dependence of a on t

We assume on the basis of the values of ω, σ, and ξ following from the S–n curves (Table II) that the intermediate products AA_2 and A_1A_2 are during the reaction up to a certain conversion in a stationary state. This was substantiated by calculating the theoretical trajectories (A_i)–(Z_1) from Eqs (4)–(8) by an analogue computer (Fig. 3). The values of ω, σ and ξ were chosen close to those in Table II, valid for 20°C and $H_0 = -3$. A stationary state of the components AA_2 and A_1A_2 exists in the reaction mixture for compound *I* ($\xi = 10$, $\omega = 100$, $\sigma = 75$) and $n = 1\cdot5$ or 2 practically in the whole range of the reaction times. During oxidation of compound *II* ($\xi = 15$, $\omega = 20$, $\sigma = 30$), this criterion holds for $n = 2$ up to about 80% conversion, for $n = 1\cdot5$ and species A_1A_2 up to about 70% and for AA_2 up to about 60% conversion. In this time interval, the a–t dependence represents naturally only the function (A_2)–t, since $a(n)/a_\infty(n = 2) = (A_2)$.

Linearization of the a–t Function

The differential kinetic equation describing the (A_2)–t function for the considered scheme (see Theoretical) with the assumption of a stationary state for A_1, AA_2, A_1A_2, and A_2A_2 has the form

$$d(A_2)/d\tau = b[k_1(A)(Z_1) + k_3(A)(A_2)].\qquad(12)$$

This equation can be solved with the conditions

$$(A) + (A_2) = 1,\quad (Z) + (Z_1) = n,\quad (Z) = 2(A_2)\qquad(13)$$

in a closed form; the result can be expressed as a special case of a general functional dependence represented by the sum of two exponentials, which can be linearized[9]. We arrive at the equation

$$Y = [\exp(\gamma\,\Delta t) + 1]\,X - \exp(\gamma\,\Delta t),\qquad(14)$$

where

$$Y = [(A_2)_\infty - (A_2)]/[(A_2)_\infty - (A_2)_2] = [a_\infty - a(t)]/[a_\infty - a(t_2)],$$
$$X = [(A_2)_\infty - (A_2)]/[(A_2)_\infty - (A_2)_1] = [a_\infty - a(t)]/[a_\infty - a(t_1)].$$

The quantities X and Y can be obtained from the *a–t* curve for a given n by determining the values of $a(t)$, $a(t_1)$, $a(t_2)$ for t, t_1 and t_2 forming an arithmetic series.
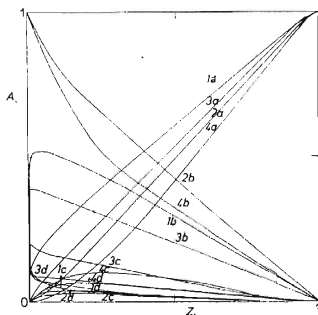

Fig. 3

Dependences of (A_1) on (Z_1) Calculated by Analogue Computer from Equations (4)—(7) and (11)

Curves *a*, *b*, *c*, and *d* represent the dependences of (A), (A_2), (AA_2) and (A_1A_2) on (Z_1), where $(A_i) = [A_i]/b$ and $(Z_1) = [Z_1]/z$. Curves *1* correspond to $\xi = 10$, $\omega = 100$, $\sigma = 75$, $n = 1\cdot5$; curves *2* as *1* but $n = 2$. Curves *3* correspond to $\xi = 15$, $\omega = 20$, $\sigma = 30$, $n = 1\cdot5$; curves *4* as *3* but $n = 2$.

The dependence (14) corresponds to a straight line in the coordinates X, Y passing through the point X = Y = 1. This linearity for a given value of n is an evidence for the validity of Eq. (12); its intersection and slope give the values of k_1 and k_3, since $\gamma = bk_3 + bk_1(n - 2)$ for $n \neq 2$ or $\gamma = bk_3$ for $n = 2$. As an example, Table III gives the values of $\xi = k_3/k_1$ for oxidation of compound I with cerium(IV) sulphate at 5°C and $H_0 = -3$, obtained from the a–t curves for various n values. The table gives also the extent of the reaction with respect to A or Z_1, up to which the X–Y dependence can be considered linear. These data and the agreement between the values of ξ from spectrophotometry and from E–t curves (Table IV) suggest the correctness of the proposed scheme.

TABLE III

Values of ξ Obtained by Linearization of the a–t Dependence with n as Parameter

Data refer to compound I and cerium(IV) sulphate at 5°C and $H_0 = -3$; r is the extent of the reaction with respect to Z_1 ($n < 2$) or A ($n > 2$), up to which the X—Y dependence is linear.

n	ξ	r
0·49	9·40	50%
0·98	10·05	73
1·48	12·10	71
1·97	9·95	72
2·46	5·04	77
2·95	15·24	73
3·44	18·83	85

TABLE IV

Ratios of Rate Constants $k_3/k_1 = \xi$ Determined from S–n Curves, by Rectification of the $[A_2]$–t Dependence and by the Analogue Computer for Oxidation of Compounds I and II at 20°C

| Compound	H_0	n	$\xi = k_3/k_1$		
			linearization	anal. comp.	S–n curve
I	—3	1·5	5	6	8
		2	4	4	
II	—3	1·5	13	8	15
		2	15	20	
	—1	2	2·1	2	5

Analogue Solution

Eq. *(12)* and the conditions *(13)* were after some modifications solved on a MEDA 42 TA type analogue computer. The fact that the absorbance of the reaction mixture does not change after exhaustion of Z_1 was taken into account in the circuiting. With the aid of the computing network in combination with a generator of the function $y = \ln \tau$ nomograms of the (A_2)–$\ln \tau$ dependence with ξ as parameter were obtained for selected values of n. Based on the agreement of the normed experimental curves (A_2)–$\ln t$ with one of the theoretical curves, the proposed scheme was substantiated and the value of ξ was determined. The difference of $\ln \tau - \ln t = \ln (bk_1)$ on the x axis of the nomogram and experimental dependence gives the value of k_1.

It follows from Table IV that a good agreement was attained among the values of ξ determined by the method of *S–n* curves, rectification, and by the analogue computer, especially if we take into account the complexness of the reaction scheme and high overall reaction rate, since the rate constant k_1, which is the smallest one, is equal to $10^2 - 10^3$ dm^3/mol s for both substances under the given conditions. Its magnitude was checked by calculation from the slope of the dependence (A_2)–t for $t \to 0$, where only the step 1 plays a role under the condition $[A_1]_{t=0} \equiv [A_2]_{t=0}$.

COMPOUND *IV*

E–t Curves

The dependence of E_∞ on n shows a potential step for $n = 2$, an evidence for a two-electron oxidation similarly to compounds *I* and *II*. The *S–n* dependence, represented in the interval $n(0; 2)$ by a decreasing straight line, suggests, however, another oxidation mechanism. Its experimental course (Fig. 2, curve *4*) can be explained either *1*) by a system of two concurrent consecutive reactions with the condition $k_1 \ll k_2$, or *2*) by the same scheme supplemented with dismutation of the intermediate product:

$$2A_1 \xrightleftharpoons[k_d']{k_d} A + A_2 ,$$
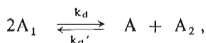
with the condition $k_d \gg k_d'$. Since the norm of the *S* axis is not known, these two cases cannot be distinguished ($S(n = 0) = 2$ for case *1*), but $S(n = 0) = 1$ for case *2*) according to ref.[4,5]). The ratio of the rate constants, k_2/k_1 or k_d/k_d', cannot be determined either. In both cases, the system behaves naturally as a second-order reaction with a stoichiometry of A : $Z_1 = 1 : 2$, so that the experimental ensemble of *E–t* curves could be used for calculating the value of k_1 in a similar way as in the case of a simple bimolecular reaction[10,11]. The result of this procedure is the value of $k_1 = 8400$ dm^3/mol s for $H_0 = -4$ and 20°C.

Spectrophotometric Measurements

Eq. (10) holds also now and the dependence of a_∞ on n is similar to that for compounds I and II. Since we consider only one intermediate product, A_1, in the stationary state, the a–t curve measured in the visible range of the spectrum represents the (A_2)–t dependence. If we assume oxidation according to case 1, we obtain by solving the differential equation $d(A_2)/dt = bk_1(A)(Z_1)$ with the conditions $(A) + (A_2) = 1$, $(Z_1) + (Z) = n$, and $(Z) = 2(A_2)$ the following expressions:

$$\ln\left[(n - 2(A_2))/(1 - (A_2))\right] = bk_1(n - 2)\,t + \ln n\,, \quad n \ne 2\,, \qquad (15)$$

$$1/(1 - (A_2)) = 1 + 2bk_1t\,, \quad n = 2\,. \qquad (16)$$

By using the experimental a–t curve for a given n and plotting the left sides of Eqs (15) and (16) against t we obtained exactly linear dependences from which the values of k_1 were obtained. These are in good agreement with the results of analysis of the E–t curves under the same conditions: $k_1 = 9780$ $(n = 1)$, 9670 $(n = 1.4)$, 9870 $(n = 2)$, 9400 $(n = 3)$ dm^3/mol s. By comparing the experimental dependences of (A_2) on $\log t$ for $n = 1$ and 2 with nomograms calculated for the same n values and case 1 by an analogue computer we obtain an average value of $k_1 = 1.02 \cdot 10^4$ dm^3/mol s.

Neither of the mentioned methods enables to distinguish the two proposed mechanisms. In case 2 with an irreversible dismutation of A_1 we obtain equations which differ from (15) and (16) only by the coefficient 0.5 in the terms containing t, provided that $d(A_1)/dt = 0$. The analogue solution showed the possibility of the same form of the (A_2)–t dependence with the condition $k_d \approx 10^3 k_1 \approx 10^7$ dm^3/mol s, or $k_2 \approx \approx 500 k_1 \approx 5 \cdot 10^6$ dm^3/mol s, or if the ratios of k_2/k_1 and k_d/k_1 are simultaneously larger than 20. In view of the high value of $k_d = 10^7$ dm^3/mol s for the reaction between two relatively large organic molecules of A_1, the reaction assumed in case I appears more probable. The necessary high rate of oxidation of A_1 to A_2 $(k_2 = = 5 \cdot 10^6$ dm^3/mol s) refers to the reaction between an organic molecule A_1 and a strong oxidising agent Ce(IV).

Compound *III*

It follows from the dependences of E_∞ and a_∞ on n that the stoichiometrical ratio of $A : Z_1$ is different from that in the case of compounds I, II and IV: it is equal to $1 : 3$. This is an evidence for a different oxidation mechanism of compound III, which will be discussed in a subsequent communication.

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