ELECTROCHEMICAL MODELING OF THE OXIDATIVE DEHYDROGENATION OF 1-PHENYL-1H-3-METHYL-6,7-DIMETHOXYISOCHROMENE

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The electrochemical oxidation of 1-phenyl-1H-3-methyl-6,7-dimethoxyisochromene on a rotating platinum disk electrode with a ring in acetonitrile was investigated. Three one-electron waves are observed on the polarization curves of the disk electrode, and three cathode waves corresponding to reduction of the intermediates are recorded on the ring. The current decreases after the second wave, and this constitutes evidence for the occurrence of a subsequent chemical reaction. It was established that decomposition of the isochromene cation radical leads to the 3-methyl-6,7-dimethoxy-2-benzo-pyrylium ion, while decomposition of the dication leads to the 1-phenyl-3-methyl-6,7-dimethoxy-2-benzopyrylium ion, which is formed via an EEP scheme.

A rather large number of studies in which the researchers were able to experimentally demonstrate the role of the acts of one-electron transfer in the mechanism of splitting out of the "hydride"-labile hydrogen atom (aromatization) have been published in recent years [1-6]. The fact that cleavage of the C_1—C'_1 bond rather than oxidative dehydrogenation to give a bispyrylium salt occurs under the influence of rather strong electron acceptors (triphenylmethyl perchlorate and acetyl perchlorate) on bisisochromenes was therefore extremely unexpected [7]. We observed a similar pattern in the oxidation of 1-phenyl-1H-3-methyl-6,7-dimethoxyisochromene (I). The final product of this reaction is also the 3-methyl-6,7-dimethoxy-2-benzopyrylium cation (II).

In the present research we made an attempt to accomplish the electrochemical modeling of the dehydrogenation of I on a rotating disk electrode with a ring [8] in acetonitrile. One might have expected that the 1-phenyl-3-methyl-6,7-dimethoxy-2-benzopyrylium (III) and 3-methyl-6,7-dimethoxy-2-benzopyrylium (II) cations would be formed as the final products of this reaction. We therefore initially studied the electrochemical behavior of these cations (Table 1).

The studies showed that cations II and III are reduced on the disk electrode in one one-electron step (the anode wave of the corresponding radicals is recorded on the ring). Moreover, despite the presence of two electron-donor groups in the benzene ring of the molecule, the cations do not undergo further oxidation up to the discharge potential of the base electrolyte.

Three one-electron waves are observed on the volt—ampere curves in the case of oxidation of I on the disk electrode (Table 2), while three corresponding cathode waves corresponding to reduction of the intermediates are observed on the ring electrode. (E_{const}^r is equal to the first wave of oxidation on the disk.)

After the second wave, the current on the ring decreases, and this constitutes evidence for the occurrence of chemical reactions after the detachment of the second electron. Recording of the volt—ampere curves on the ring ($E_{const}^r = -0.75$ V) with a potential corresponding to the start of the plateau of the limiting current for the reduction of cations II

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TABLE 1. Electrochemical Behavior of Derivatives of the 2-Benzopyrylium Cation (II, III) and Tetramethyl-p-phenylenediamine (XI) on a Rotating Disk Electrode with a Ring in Acetonitrile

Compound	Electrode	E_{const}, V	$E_{1/2}$, V	i_{lim}, μA	n^a	Q^b, %
II	Disk	—	−0,61	28,0	0,95	—
	Ring	$E^r = -0{,}40$	−0,61	0,016	—	0,4
III	Disk	—	−0,54	27,0	0,99	—
	Ring	$E^r = -0{,}35$	−0,53	0,01	—	0,2
XI	Disk	—	+0,12	35,0	1,0	—
	Ring	$E^r = -0{,}03$	+0,12	5,5	—	100

[a] This is the number of electrons transferred. [b] This is the coefficient of the yield with respect to the current.

TABLE 2. Electrochemical Oxidation of 1-Phenyl-1H-3-methyl-6,7-dimethoxyisochromene on a Rotating Disk Electrode with a Ring in Acetonitrile

Electrode	E_{const}, V	$E'_{1/2}$, V	i'_{lim}, μA	n/Q, %	$+E''_{1/2}$, V	i''_{lim}, μA	n/Q, %	$+E'''_{1/2}$, V	i'''_{lim}, μA	n/Q, %
Disk	—	+0,83	26,4	$0{,}88^a$	1,27	25,3	$0{,}85^a$	1,42	24,7	$0{,}82^a$
Ring	$E^r = +0{,}65$	+0,80	0,06	$1{,}45^b$	1,22	0,14	$3{,}52^b$	1,42	0,13	$3{,}35^b$
Ring	$E^r = -0{,}75$	+0,82	4,2	101^b	1,26	4,1	103^6	1,38	4,1	106^b
Ring	$E^d = +1{,}00$	−0,59	4,3	104^b	—	—	—	—	—	—
Ring	$E^d = +1{,}37$	−0,62	8,0	99^b	—	—	—	—	—	—
Ring	$E^d = +1{,}50$	−0,55	11,0	99^b	—	—	—	—	—	—

[a] This is the number of electrons transferred. [b] This is the coefficient of the yield with respect to the current.

or III or of the protons [5] showed that a total of three electrons are consumed in the reduction of the products formed on the disk. A wave of reduction of cation II is observed on the polarization curves recorded on the ring electrode with a constant potential of the disk (E_{const}^d) equal in value to the start of the plateau of the limiting current of the first wave of oxidation of isochromene I. When E_{const}^d is equal, respectively, to the potentials of the plateaus of the current of the second and third waves, the polarization curves are the sum of the unseparated waves, which, with respect to the current, correspond to the transfer of two and three electrons.

The data obtained make it possible to propose the following scheme of possible transformations of isochromene I during oxidation.

Let us examine the probability of the occurrence of the reactions presented in the scheme. Detachment of the first electron from I leads to cation radical IV, which then undergoes decomposition (2) to give a phenyl radical and cation II. The one-electron character of the first wave indicates that the phenyl radical is not oxidized (1) under these conditions. The low stability of cation radical IV and the character of its decomposition (the half-conversion time estimated by the method in [9] is $2 \cdot 10^{-3}$ sec) are probably due to steric factors. In the case of 2,4,6-tri-tert-butyl-4H-pyran even the EPR spectrum of its cation radical was obtained [6].

Since preliminary studies showed that cations II and III are not oxidized over the investigated range of potentials, the second wave corresponds to the reversible transfer of yet another electron (5) from cation radical IV (similar phenomena were observed in the oxidation of 9-cyanoacridan [5]). Dication V in turn can undergo decomposition with the detachment of a proton [(5) and (4)], and the final product will then be cation III. In addition, another reaction pathway [(5) and (6)] is also possible. In both the (5) and (4) case and the (5) and (6) case the process corresponds to the overall transfer of two electrons. However, if detachment of a phenyl cation from dication V (6) were to occur, as a consequence of its low stability on the ring electrode (E_{const}^r = −0.75 V), the current of the second

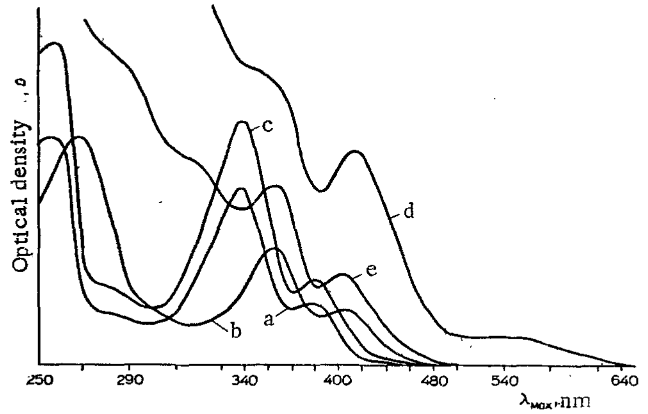
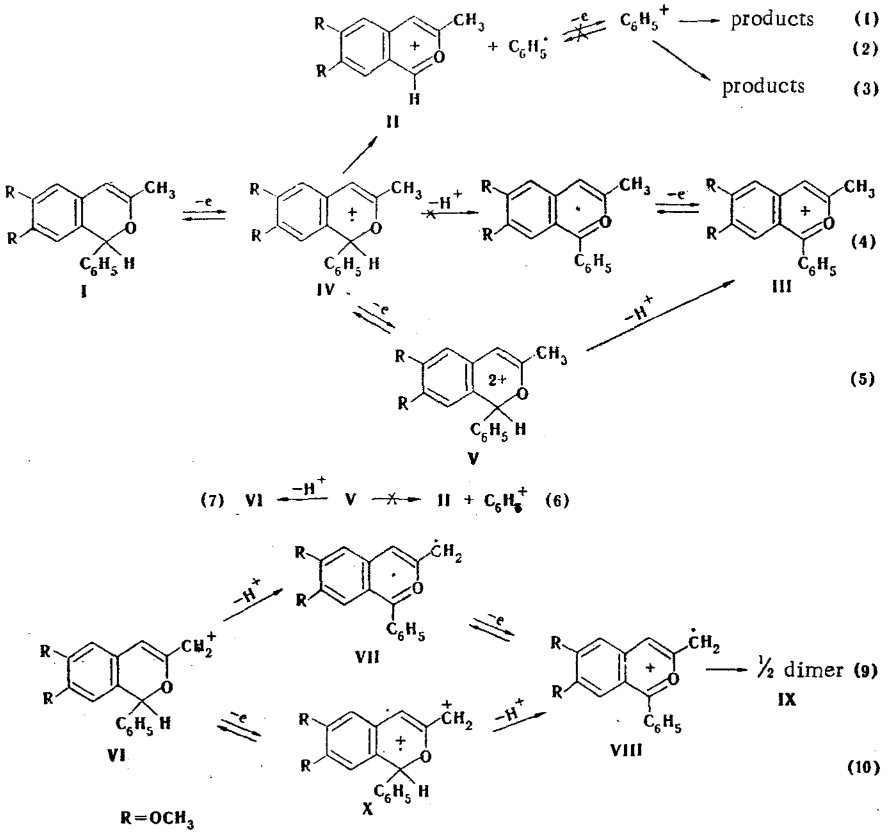


Fig. 1. Electronic absorption spectra of model cations II and III and the products of oxidation of isochromene I in acetonitrile: a) the 3-methyl-6,7-dimethoxy-2-benzopyrylium ion; b) the 1-phenyl-3-methyl-6,7-dimethoxy-2-benzopyrylium cation; c) product of oxidation of isochromene I at a potential corresponding to the transfer of the first electron; d) the same as spectrum c at the potential of transfer of the second electron; e) the same as spectrum c at the potential of transfer of the third electron.



wave would have a much smaller value (Table 2). The (5) and (4) pathway is therefore more likely. (The second wave on the ring corresponds to reduction of a proton [5].)

As we have already noted, yet a third one-electron wave with a preceding chemical reaction is observed in the oxidation of isochromene I. It might be assumed that deprotonation of the methyl group (7), as was observed in the oxidation of substituted toluenes [10], occurs in addition to reactions (5) and (6). After this, cation VI can undergo transformations via (8) and (9) or (9) and (10). A third one-electron wave corresponding to the reduction of yet another proton should then be recorded on the ring electrode, and this is, in fact, observed experimentally (Table 2). It is difficult to make a choice between reactions (8) and (9) and (9) and (10) on the basis of the available experimental data, although the formation of dication radical X seems less likely than the formation of diradical VII.

To identify the final products of the oxidation of isochromene I we carried out its preparative electrolysis in a circulation cell [11] with subsequent recording of the electronic absorption spectra of the reaction solutions. It is apparent from Fig. 1 that the principal product at an anode potential corresponding to the plateau of the limiting current of the first wave (E^a = +1.0 V) is 2-benzopyrylium cation II. A mixture consisting of substituted 1-phenyl-2-benzopyrylium cation III and hypothetical dimer IX is formed in two other cases (E^a = +1.35, E^a = +1.50 V).

Thus the studies showed that, depending on the anode potential, the oxidation of isochromene I may lead both to substituted 2-benzopyrylium cation II and to oxidative dehydrogenation and the formation of substituted 1-phenyl-2-benzopyrylium cation III with the successive transfer of two electrons and a proton (EEP scheme). In all likelihood, in the chemical reaction the formation of substituted 2-benzopyrylium cation II is associated with the relatively low reduction potentials of the electron acceptors used [12].

EXPERIMENTAL

Pure-grade acetonitrile was purified immediately prior to the preparation by the method in [13]. A 0.1 N solution of tetra-n-butylammonium perchlorate was used as the base electrolyte. A saturated aqueous calomel electrode served as the reference electrode.

1-Phenyl-1H-3-methyl-6,7-dimethoxyisochromene (I). An ether solution of a Grignard reagent (0.03 mole) was added dropwise to 3 g (0.01 mole) of 3-methyl-6,7-dimethoxy-2-benzopyrylium perchlorate in 10-15 ml of absolute ether, and the reaction mixture was refluxed with stirring in a water bath for 1 h, during which a light-brown precipitate formed. The reaction mixture was then treated with a saturated solution of NH_4Cl, and the ether layer was separated, washed with water, and dried with anhydrous sodium sulfate. The ether was removed by distillation, and the residue was recrystallized from ethanol to give 2.2 g (78%) of colorless crystals with mp 69°C. IR spectrum: 1020, 1040, 1235, 1280, 1580, 1610, 1660 cm^{-1}. PMR spectrum (in CCl_4): 1.75 (CH_3); 3.50 and 3.65 (two CH_3O); 5.3, 5.82, 6.05, and 6.26 (CH); 7.17 ppm (C_6H_5). Found: C 76.3; H 6.4%. $C_{18}H_{18}O_3$. Calculated: C 76.6; H 6.4%. Cations II and III were obtained by the method in [7].

The method used to record the volt-ampere curves on the rotating disk electrode and its construction and preparation are described in [14]. The electrode had the following characteristics: r_1 = 1.00 mm, r_2 = 1.04 mm, r_3 = 1.07 mm, and n = 3000 rpm; the coefficient of efficiency calculated from the results obtained in the oxidation of tetramethyl-p-phenylenediamine was 0.157. The number of electrons transferred on the disk electrode was calculated from the assumption that the coefficients of diffusion of the depolarizers were inversely proportional to the square root of the molecular mass. The concentration of the compounds was $5 \cdot 10^{-4}$ mole/liter.

Preparative electrolysis was accomplished in an electrolyzer of the type in [11] with a P-5827M potentiostat. The concentration of isochromene I was $5 \cdot 10^{-4}$ mole/liter. The electronic absorption spectra were recorded with a Hitachi EPS-3T spectrophotometer.

LITERATURE CITED

1. I. M. Sosonkin and G. L. Kalb, Zh. Org. Khim., 10, 1333 (1974).
2. I. M. Sosonkin, V. A. Subbotin, V. N. Charushin, and O. N. Chupakhin, Dokl. Akad. Nauk SSSR, 229, 888 (1976).
3. O. V. Drygina, G. N. Dorofeenko, and O. Yu. Okhlobystin, Khim. Geterotsikl. Soedin., No. 9, 1172 (1977).
4. E. Sturm, H. Kiesele, and E. Daltrozzo, Chem. Ber., 111, 227 (1978).
5. I. M. Sosonkin, O. N. Chupakhin, and A. I. Matern, Zh. Org. Khim., 15, 1976 (1979).
6. O. Yu. Okhlobystin, V. A. Samarskii, M. V. Nekhoroshev, and V. D. Pokhodenko, Zh. Org. Khim., 15, 1110 (1979).
7. G. N. Dorofeenko, G. P. Safaryan, V. F. Voloshinova, and O. Yu. Okhlobystin, Khim. Geterotsikl. Soedin., No. 7, 999 (1976).

8. A. N. Frumkin and L. N. Nekrasov, Dokl. Akad. Nauk SSSR, 126, 115 (1959).
9. W. J. Albery and S. Bruckenstein, Trans. Faraday Soc., 62, 1946 (1966).
10. L. Eberson and K. Nyberg. J. Am. Chem. Soc., 88, 1686 (1966).
11. I. M. Sosonkin and A. N. Domarev, Élektrokhimiya, 8, 1168 (1972).
12. H. Volz and W. Lotsch, Tetrahedron Lett., 2275 (1969).
13. I. M. Sosonkin, A. N. Domarev, É. G. Kaminskaya, A. I. Tolstikov, F. F. Lakomov, and A. Ya. Kaminskii, Zh. Prikl. Khim., 44, 950 (1971).
14. I. M. Sosonkin, V. A. Subbotin, and N. V. Fedyainov, Zh. Org. Khim., 15, 344 (1979).

SYNTHESIS AND THREE-DIMENSIONAL STRUCTURE OF 5,5-DISUBSTITUTED 2-ALKOXY-1,3-DIOXANES

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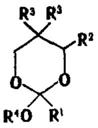
It was established by PMR spectroscopy that a chair conformation with an axial orientation of the alkoxy substituent is the primary conformation for 5,5-disubstituted (and unsubstituted) 2-alkoxy-1,3-dioxanes. As compared with alkyl-1,3-dioxanes, 2-alkoxy-1,3-dioxanes are characterized by reversal of the chemical shifts of the axial and equatorial protons attached to C_4 and C_6.

Little study has been devoted to the stereochemical peculiarities of 2-alkoxy-1,3-dioxanes. Only several studies [1-4] in which the conformational equilibria of a number of 4-, 4,6-, and 4,4,6-methyl-substituted 2-methoxy-1,3-dioxanes are known.

We have synthesized a number of 2-alkoxy-1,3-dioxanes with the general structure I-IX:



I-IX

I $R^1=R^2=H$, $R^3=CH_3$, $R^4=C_2H_5$; II $R^1=R^2=H$, $R^3=CH_3$, $R^4=n\text{-}C_3H_7$; III $R^1=R^2=H$, $R^3=CH_3$, $R^4=i\text{-}C_3H_7$; IV $R^1=R^2=H$, $R^3=CH_3$, $R^4=n\text{-}C_4H_9$; V $R^1=R^2=H$, $R^3=CH_2Cl$, $R^4=C_2H_5$; VI $R^1=R^2=R^3=H$, $R^4=C_2H_5$; VII $R^1=R^2=R^3=H$, $R^4=i\text{-}C_3H_7$; VIII $R^1=R^4=CH_3$, $R^2=R^3=H$; IX $R^1=R^2=CH_3$, $R^3=H$, $R^4=C_2H_5$

The configurations and primary conformations of dioxanes I-IX were determined by an analysis of the character of the multiplet splitting and the chemical shifts of the resonance lines of the protons in the PMR spectra of 10% solutions of these compounds in carbon tetrachloride, deuteroacetone, and deuterochloroform.

It is generally accepted that a chair conformation with an axial orientation of the alkoxy group is the preferred conformation in 2-alkoxy-1,3-dioxanes [1-6].

In the PMR spectra of I-V (Table 1), as a consequence of a shift of the conformational equilibrium to favor a certain primary conformation, the protons of the methylene groups in the equivalent 4 and 6 positions give a typical AB quartet with a geminal constant of −11.0 Hz. The magnitude of the $^2J_{ae}$ constant and the rather great magnetic nonequivalence of the axial and equatorial protons of these groups ($\Delta\delta$ = 0.4-0.5 ppm) constitute evidence for a chairlike conformation of the ring [7-10].

In contrast to alkyl-1,3-dioxanes [8], the axial protons attached to C_4 and C_6 resonate at weaker field (δ 3.65 ppm for I-IV and 3.95 ppm for V) than the equatorial protons (δ 3.16-3.20 ppm and 3.57 ppm, respectively). The reversal of the constants of shielding of the H_a

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