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POLAROGRAPHIC REDUCTION OF PYRYLIUM SALTS

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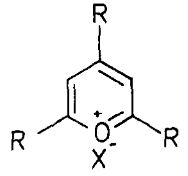
Abstract - The polarographic reduction of several pyrylium perchlorates in buffered and unbuffered solution was investigated at DME. In 0.1M LiCl-DMF, two waves are observed. The first wave is reversible and diffusion controlled representing the uptake of one electron, whereas the second wave is a catalytic reduction of the perchlorate ion. In buffered solutions (pH $\leqslant$ 5), only one wave is obtained and its i_l decreases with pH due to the partial conversion of the pyrylium salt into a pseudo-base. The rate of conversion, electron affinities, ionization potentials and the energy levels of HOMO and LUMO of these compounds have been computed and a linear correlation shown to exist between the spectroscopic data and the redox potentials.

The polarographic reduction of pyrylium salts and tropylium salts has attracted the attention of many authors[1-14]. Balaban[4] reported preliminary polarographic results for some pyrylium salts. Two waves are observed in non-buffered solutions, the first representing the uptake of one electron, while the second was not dealt with. To better understand the electrode processes of pyrylium salts further polarographic studies are needed. The present work investigates the nature of the different waves, the dependence of $E_{1/2}$ on pH and the rate of reduction for several substituted pyrylium salts.



(R = Me, Et or Ph); (X = I or ClO_4)

The different kinetic parameters have also been mathematically treated to show a correlation between the spectroscopic and the electrochemical data.

EXPERIMENTAL

The pyrylium salts (Table 1) were prepared according to the procedure described by Balaban[15,16]. Purities were checked by m.p. determination, elemental analysis and I.R. spectra. The polarograms were recorded by Radiometer PO_4 type recording polarograph using a dropping electrode (m = 2.71 mg/s and t = 4.35 s at a mercury height of 50 cm) and a Kalousek polarographic cell with a thermostating jacket. The temperature was maintained at 25 ± 0.1°C using an ultrathermostat. A saturated calomel electrode (SCE) was used as reference electrode. Buffers used were sodium acetate-HCl, since phosphate buffers apparently react with pyrylium salts[7]. A Radiometer pH meter type 63 fitted with a combined glass electrode type GK 2301 C was employed for determination of pH. Electrolysis at controlled potential was made using a potentiostate (TACUSSEL ASA 4/60). The electrolytic cell used was the same as that described by Peltier[17]. The U.V. absorption spectra were recorded in DMF on a Pye Unicam SP 1800 spectrophotometer attached to a temperature regulated cell holder. The parameters used for SCF-PPP-CI quantum chemical approximation were taken from literature[18]. Details of the calculations were the same as described before[19].

RESULTS AND DISCUSSION

Behaviour in non-buffered solutions. The polarographic reduction of $1x10^{3}$M 2,4,6-triphenylpyrylium perchlorate in 0.1M LiCl-DMF as supporting electrolyte was investigated first. The polarogram consists of two waves at -0.301 and -1.403 V with a height ratio of ~ 1:6.3. The first wave is diffusion controlled as the slope (x) of log i-log h was 0.52 obeing Ilkovic equation. The second wave is diffusion with a partial contribution of adsorption where the slope (x) = 0.59 and the values of i_{ℓ}/C were not constant. No explanation has been reported regarding the nature of the second wave which is observed in non-buffered solution.

Since only pyrylium perchlorates show the second wave, this excludes the possibility that such a wave may represent a catalytic hydrogen wave or a successive reduction of pyrylium moiety. Therefore, the second wave appears evidently to be assigned as a catalytic reduction of the perchlorate ion, a conclusion which is supported by a study of the effect of $NaClO_4$ concentration (dissolved in DMF) on the electroreduction of 2,4,6-triphenylpyrylium perchlorate at a DME (Fig. 1). The height of the second wave was found to increase as the concentration of $NaClO_4$ is increased; subsequently the $E_{1/2}$ of this wave shifted toward less negative potentials. The same trend with almost the same result is also observed in the case of 2,4,6-trimethylpyrylium perchlorate, Fig. 2. To throw more light on the nature of this second wave, the polarographic reduction of 2,4,6-triphenylpyrylium iodide was investigated. The results are illustrated in polarogram (a) in Fig. 3. The polarogram consists of only one wave at -0.404 V. On adding small amounts of $NaClO_4$, a second wave starts to appear at -1.4 V, its height being increased as the concentration of $NaClO_4$ is increased. However, no reduction wave could be observed upon successive addition of $NaClO_4$ to a

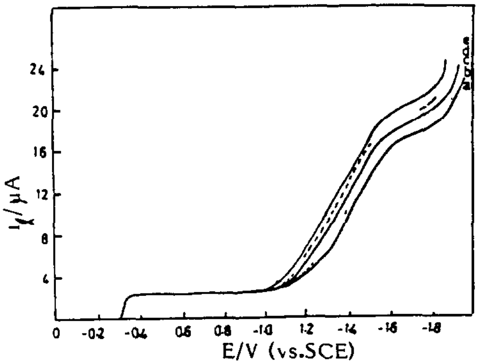


Fig.1. The effect of $NaClO_4$ concentrations on the polarographic behaviour of 1mM 2,4,6-triphenylpyrylium perchlorate in 0.1M LiCl-DMF.
a) 0 0,b) 0.5, c) 1 0,d) 2.0, e) 4 0x10^{-4}M.

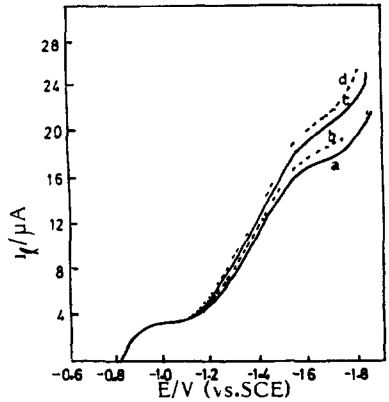


Fig.2. The effect of $NaClO_4$ concentrations on the polarographic behaviour of 1mM 2,4,6-trimethylpyrylium perchlorate in 0.1M LiCl-DMF.
a) 0.0, b) 0.5, c) 1.0, d) $4x10^{-4}$M.

solution of 0.1M LiCl-DMF and in the absence of pyrylium salt. All these results lead us to believe that the second wave represents the polarographic reduction of perchlorate ion which is catalysed by the presence of pyrylium ion.

On the other hand, the first wave represents the reduction of pyrylium ion and corresponds to a one electron process[4,8]. Coulometric analysis under controlled potential and a μ of 0.1, with application of the Ilkovic equation, showed that the first wave corresponds to a one electron process. The diffusion coefficient of the depolarizer was determined from the molar volume by applying the Stokes-Einstein relation (1).

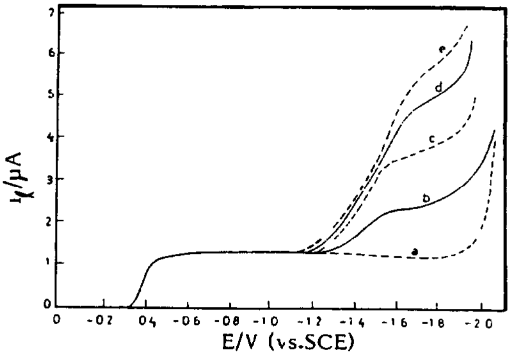


Fig. 3. The effect of $NaClO_4$ concentrations on the polarographic behaviour of 0.5 mM 2,4,6-triphenylpyrylium iodide in 0.1M LiCl-DMF.

a) 0.0, b) 0.3, c) 0.5, d) 1.2, e) $2x10^{-4}$M

$$(1)\ D_o = 3.31x10^{-5}\ (D/M)^{1/3}/\eta\ \ cm^2\ sec^{-1}$$

The values of the diffusion coefficient (D) obtained by this method are reported in Table 1.

Behaviour in buffered solutions. As pyrylium salts hydrolyse readily in basic or slightly acidic media yielding tautomeric pseudo-bases[7,10], the polarograms in buffer solutions were recorded directly after one minute of mixing. Fig 4 represents polarograms of $1x10^{-3}$M 2,4,6-triphenylpyrylium perchlorate in 50% (V/V) ethanol-acetate buffer solutions of pH 0.8 to 5. The polarogram consists of one reversible reduction wave, its limiting current suffers a marked decrease as the pH is increased without variation of the half-wave potential. The same behaviour which is also observed with other pyrylium salts, indicates that no proton is involved in the electroreduction process. The decrease in the limiting current may be due to the decrease of the bulk concentration of the pyrylium salt which undergoes partial conversion to a pseudo-base. At pH > 5, complete conversion of the pyrylium ion into the pseudo-base occurs and the solution becomes orange in colour.

The rate of conversion of the pyrylium ion into the pseudo-base has been investigated polarographically Polarograms (Fig. 5) show the effect of time on the electroreduction

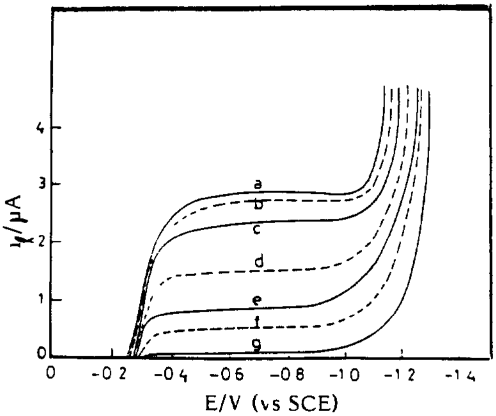


Fig. 4. Polarograms of 1mM of 2,4,6-triphenylpyrylium perchlorate in 50% ethanol-acetate-buffer solutions.

a) pH 0.8, b) 1.2, c) pH 3, d) pH 4.3 e) pH 4.6, f) pH 4.8, g) pH 5.0

of 2,4,6-triphenylpyrylium perchlorate in acetate buffer at pH 3 and 4.3. The total limiting current is completely suppressed after 190 min at pH 3 and after 45 min. at pH 4.3. The solution then turns orange, indicating complete conversion into the pseudo-base. The conversion rate is a first order reaction with respect to the pyrylium ion. The rate constant k increases from 0.012 to 0.046 min^{-1} as the pH is increased from 3 to 4.3, i.e. the rate is accelerated by OH^- ions. It was found that the presence of phenyl groups in the pyrylium ring enhances the rate of conversion more than with the alkyl substituted groups; k of trimethyl substituted = 0.029 min^{-1} at pH 4.3. On the other hand, the reverse conversion of pseudo-base into pyrylium ion was found to depend on H^+ ions[10]. Thus, to the pseudo-base formed at pH 4.3, calculated amounts of HCl were added with the aim of reaching pH ca. 0.8 at which the polarographic behaviour was followed up kinetically. In this respect, it was found that the limiting current increased with time, reaching a maximum after 70 min. The rate constant was found to be 0.035 min^{-1}.

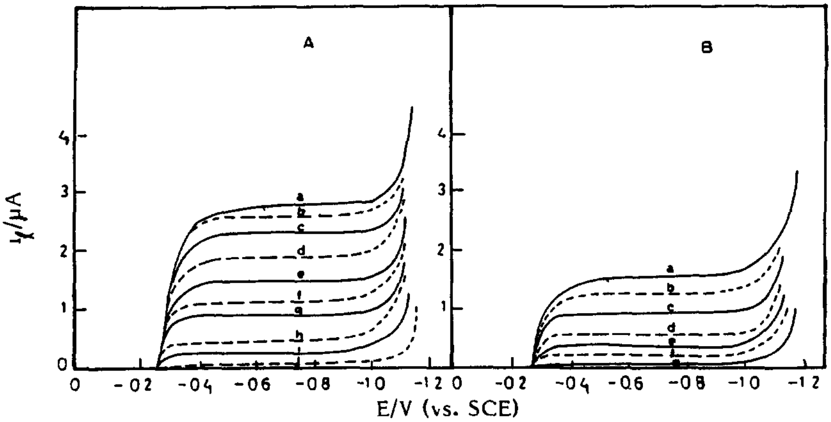
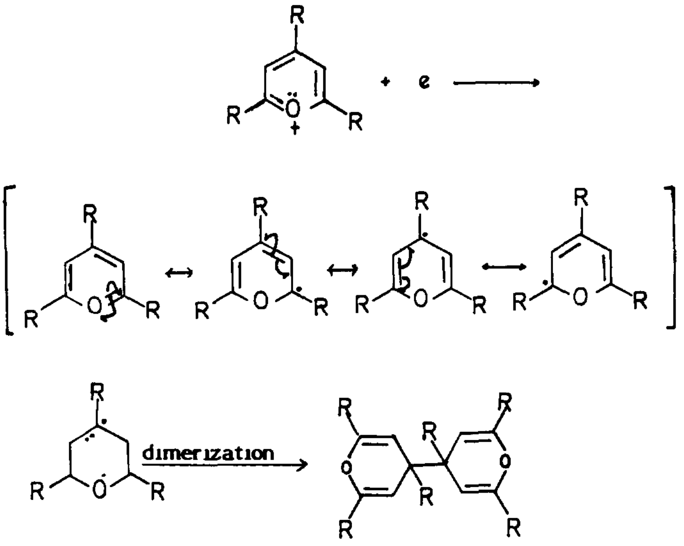


Fig. 5. Polarograms of 1mM 2,4,6-triphenylpyrylium perchlorate in 50% ethanol-acetate buffer at pH 3 (A) and at pH 4.3 (B) after various reduction times.
(A): a) 0.0 min., b) 10 min., c) 20 min., d) 40 min., e) 60 min., f) 80 min., g) 110 min., h) 150 min., i) 190 min., j) 200 min.
(B): a) 0.0 min., b) 5 min., c) 10 min., d) 20 min., e) 30 min., f) 45 min., g) 50 min

Reduction mechanisms. Pyrylium salts are easily reduced chemically; the products of reduction depend on the nature of the reducing agent. When Zn dust is used as a reducing agent the product formed is the dimer hexasubstituted bipyran[7]. Sodium borohydride converts pyrylium salts into a mixture of dienones and 4H-pyrans[5]. Accordingly, in order to identify the nature of the product produced at DME in our present study, it seemed necessary to compare the extracted compound with that obtained by chemical reduction using different reducing agents. The results indicated the formation of the dimer product as structurally confirmed via elemental analysis, molecular weight determination, melting point, I.R. and U.V. spectra. Furthermore, the reversibility of the reductive dimerization was investigated by treating the extracted product of the coulometric analysis with chromium trioxide and perchloric acid at 60°C. Upon cooling this mixture, 2,4,6-trisubstituted pyrylium perchlorate was found to precipitate as was confirmed by its $E_{1/2}$ and I.R. spectrum.

According to the above argument, the reduction of pyrylium salts at DME represents the uptake of one electron forming a free radical which undergoes dimerization. This suggests that pyrylium salts are similar to tropylium salts in their polarographic behaviour[9,20]. Based on the present experimental results, the speculated reduction mechanism may take place as follows:



2,2',4,4',6,6'-hexasubstituted 4,4'-bi-4H-pyran

The exclusive linking of the two pyran radicals in γ-position is probably due to the enhanced stability of the symmetric 2,4,6-trisubstituted-4H-pyran-4-yl resonance structure.

Determination of electron affinities, ionization potentials and molecular orbital energies. Consulting the half-wave potentials of pyrylium salts in 0.1M LiCl-DMF (Table 1), one can conclude that an increase of the donor character of the substituent makes the reduction wave shift to more negative potentials. Analysis of the waves[21] (Table 1) indicates that the pyrylium wave proceeds reversibly. If the potential determining step in the polarographic reduction of a compound is assumed to be the reversible addition of an electron to the molecule, then the half-wave reduction potential is a measure of the electron affinity (EA) of the compound under investigation. Under these conditions equation (2) can be used to calculate the EA values from half-wave reduction potentials vs. the saturated calomel electrode[22-29].

$$\text{(2)}\quad EA = E^{R}_{1/2} + 2.49 \pm 0.26\ \text{eV}$$

On the other hand, the half-wave oxidation potentials of organic compounds may be (within certain limits) directly related to the ionization potentials (IP)[30-34] according to equation (3).

$$(3)\ \mathrm{IP} = (1.478 \pm 0.027)\ E^{ox}_{1/2} + 5.821 \pm 0.009\ \mathrm{eV}$$

Values of EA and IP, calculated from equations (2) and (3), are listed in Table 1.

Table 1. Physical Characteristics of Several Pyrylium Salts in 0.1M LiCl-DMF

No.	Substituent in Position			Anion	$D \times 10^6$ (cm²/sec)	Slope of $\frac{\log(i/i_d - i)}{E}$	αn_a	$-E^R_{1/2}$ (V)	EA (eV)	E_{LUMO} (eV)	$-E^{ox}_{1/2}$ (V)	IP (eV)	$-E_{HOMO}$ (eV)	$\Delta E_{1/2}$ (V)	E_T (eV)
	2	4	6												
1	Me	Me	Me	ClO_4	3 93	16 14	0 97	0 870	1 62	0 251	0 420	5 20	0 211	0 450	4 350
2	Et	Me	Et	ClO_4	3 81	15 80	0 95	0 770	1 72	0 239	0 410	5 22	0 199	0 360	4 319
3	Me	Me	Ph	ClO_4	3 53	16,91	0 99	0 530	1 96	0 210	0 310	5 36	0 089	0 220	3 594
4	Ph	Ph	Ph	I	3 71	17 21	1 03	0 404	2 09	0 194	0 280	5 41	0 057	0 124	3 315
5	Ph	Ph	Ph	ClO_4	3 76	16 63	0 99	0 301	2 19	0 182	0 264	5 44	0 038	0 037	3 036
6	Me	Et	Me	ClO_4				(0 861)[a]	1 62	0 250	(0 454)[b]	5 15	0 248	0 407	4 341 (4 329)[c]
7	Me	Ph	Ph	I				(0 409)[a]	2 08	0 195	(0 283)[b]	5 40	0 060	0 126	3 314 (3 322)[c]

(a) Calculated using equation (4)
(b) Calculated using equation (5)
(c) Calculated using equation (6)

Maccoll[35] was the first to point out that reversible polarographic oxidation and reduction could be related to the energy of the highest occupied (E_{HOMO}) and lowest unocuupied (E_{LUMO}) molecular orbitals. The orbital energies are also related to the gas phase ionization potential as well as to the electron affinity of the molecule[36]. In this context, applying quantum chemical calculations using the well known SCF-PPP-CI MO method; the calculated parameters of interest are given in Table 1. It is worth mentioning that when the energy of HOMO increases, the compound becomes more easily oxidized and whend the energy of LUMO decreases, the compound becomes easier to be reduced. The calculated values of HOMO and LUMO for the studied compounds run in harmony with the experimentally determined values of $E_{1/2}$, IP and EA Alternatively, it is of interest to correlate the transition energy (E_T) of the longest wavelength as measured in DMF with the absolute difference between $E^{ox}_{1/2}$ and $E^R_{1/2}$. Analysis of these data by using the least square method results in the following linear equations, with an excellent correlation coefficient (r);

$$(4)\quad E_{LUMO} = -0.122\ E^R_{1/2} + 0.145, \quad r = 0.992$$

$$(5)\quad E_{HOMO} = 1\ 102\ E^{ox}_{1/2} + 0.252, \quad r = 0.997$$

$$(6)\quad E\ (E^{ox}_{1/2} - E^R_{1/2}) = 0.279\ E_T - 0.801, \quad r = 0.983$$

The validity of equation(6) is tested by calculating E_T for other pyrylium salts which are not included in the investigated series. The results show good agreement between the calculated values and those measured experimentally (c.f. Table 1).

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