ONE-ELECTRON TRANSFER REACTIONS OF PYRYLIUM CATIONS#

Dan Fărcaşiu,[a*] Alexandru T. Balaban,[b] and Ursula L. Bologa[b]

[a]*Department of Chemical Engineering, University of Pittsburgh, 1249 Benedum Hall, Pittsburgh, PA 15261, USA*
[b]*Department of Organic Chemistry, Polytechnic University of Bucharest, Spl. Independentei 313, 77206 Bucharest, Romania*

Abstract - One- and two-step one-electron transfers to pyrylium cations, generating pyranyl free radicals and anions, respectively, as well as one-electron transfers from pyrylium ions, forming dication radicals, and the properties of these species are critically reviewed.

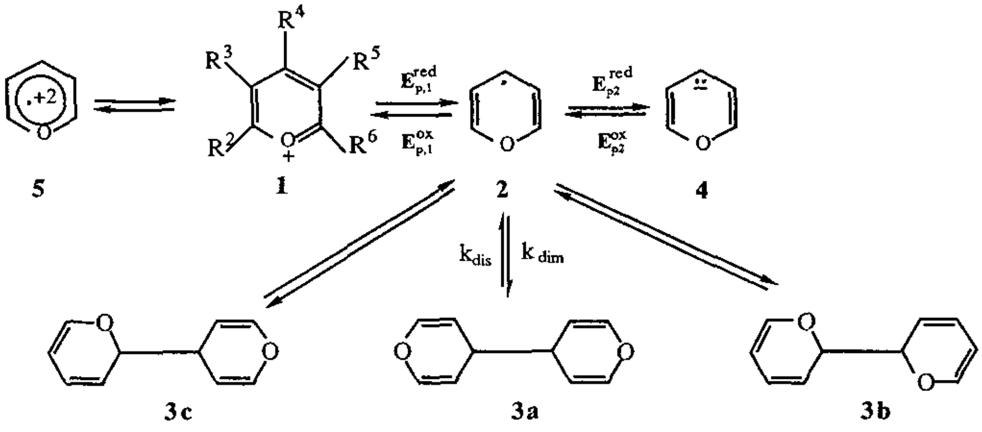
Contents

#*Dedicated to Professor Alan R. Katritzky on his 65th anniversary*

1. INTRODUCTION

"The addition of vanadous chloride to a solution of triphenylpyrylium chloride causes the formation of a reddish precipitate which (..) behaves like a free radical; (..) a chloroform solution of it is bright red and the color disappears when the solution is shaken with air. The substance is reoxidized to the pyrylium salt by ferric chloride; (..) these facts clearly indicated that we were dealing with a free radical." The paragraph above, written by Conant[1] in 1923, is remarkable in its insight, but it came much ahead of its time.[2] It took thirty years and the advent of polarography for the next studies on the reduction of benzopyrylium[3,4] and monocyclic pyrylium derivatives (1)[5] to be published. The pace of activity quickened considerably afterwards, both in the number of investigated compounds and applied methodology. Studies of the free radicals formed by reduction (2), their stability and dimerization (to 3) were undertaken. Later on, the addition of a second electron to the pyranyl free radicals, which leads to the formation of the corresponding pyranyl anions (4), and the oxidation of the parent pyrylium cations to dication radicals (5) were reported. The transformations are summarized in Scheme 1. Polarography, cyclic voltammetry, uv, ir, and esr spectroscopy proved to be useful tools for the elucidation of thermodynamic and kinetic aspects of the above reactions.

Scheme 1. One-electron transfer reactions of pyrylium heterocycles.



(For simplification, the substituents were ommitted from formulae 2-5)

A number of review articles,[6] book chapters,[7] and books[8] on pyrylium salts have been published over the last 15 years. Syntheses, physical and chemical properties, and applications were extensively discussed. The one-electron transfer reactions received, however, only a cursory treatment. It is the purpose of this article to systematize the literature on this topic for the first time. Most attention will be devoted to monocyclic cations, but relevant work on benzo analogs and isoelectronic systems with different heteroatoms will also be mentioned.

2. ONE-ELECTRON REDUCTION OF PYRYLIUM SALTS TO PYRANYL RADICALS

2.1. Electrochemical reduction

The first reports[5,9] on the *polarographic reduction* of 2,4,6-trisubstituted pyrylium cations in aqueous acidic media revealed the most important features of the one-electron transfer of these compounds: i) the electron transfer is diffusion controlled; ii) the electron transfer is reversible; iii) the $E_{1/2}$ values do not depend on anion[10,11] and pH (unless conversion to pseudobase occurs). The reduction is similar to that of tropylium.[12,13] These conclusions were confirmed in later works;[14] findings of variation in $E_{1/2}$ with the counterion[15,16] might be due to the measurements being conducted in non-buffered solutions.

An observation of linear correlation of $E_{1/2}$ with the the longest wavelength uv absorption frequency[5,16] was found to hold only for rings bearing at least one phenyl substituent.[17,18] Considering that $E_{1/2}$ is determined by LUMO energy and the uv absorption by the LUMO-HOMO gap,[19,20] such a correlation is coincidental.

The dimerization step in Scheme 1 was demonstrated for the 2,4,6-trimethylpyrylium cation (**1**, $R^2 = R^4 = R^6 = Me$, $R^3 = R^5 = H$, cf. **6** in Table 1) by isolation of the corresponding dimer and its reversion to **6** upon electrochemical oxidation. No 2,2'- or 2,4'-dipyrans (**3b** or **3c**) were detected.[9]

Following the original investigation of Balaban *et al.*[5,9-11] a sizable number of polarographic reduction potentials were reported. Most of them are collected in Table 1. An unfortunate feature of these data is the large

Table 1. Polarographic reduction potentials of pyrylium salts.

A. Alkyl substituted pyrylium salts.

Nr.	R^2	R^3	R^4	R^5	R^6	Anion	Medium	Method	$E_{1/2}$ (V) *vs.* S.C.E.	$E_{1/2}$ (V) *vs.* S.C.E.	ν UV (cm^{-1})	Ref.
6a	Me	H	Me	H	Me	ClO_4	acetate buffer	pol.	-0.870		35090	5
6a	Me	H	Me	H	Me	ClO_4	acetate buffer	pol.	-0.850			13
6a	Me	H	Me	H	Me	ClO_4	1M HCl	pol.	-0.835			18
6a	Me	H	Me	H	Me	ClO_4	acetonitrile	pol.	-0.770			32
6a	Me	H	Me	H	Me	ClO_4	acetonitrile	pol.[b]	-0.980			22
6a	Me	H	Me	H	Me	ClO_4	DMF	pol.	-0.870			15
7a	Me	H	Et	H	Me	ClO_4	acetate buffer	pol.	-0.865		35090	5
7a	Me	H	Et	H	Me	ClO_4	DMF	pol.	-0.861			16
8a	Et	H	Me	H	Et	ClO_4	acetate buffer	pol.	-0.780		34840	5
8a	Et	H	Me	H	Et	ClO_4	DMF	pol.	-0.770			16
9a	*i*-Pr	H	Me	H	*i*-Pr	ClO_4	acetate buffer	pol.	-0.739		34720	5
10a	*c*-Pr	H	Me	H	Me	ClO_4	1M HCl	pol.	-0.835		32260	18
11a	*c*-Pr	H	Me	H	*c*-Pr	ClO_4	1M HCl	pol.	-0.840		30210	18
12a	*t*-Bu	H	H	H	*t*-Bu	ClO_4	acrylonitrile	pol.[b]	-0.740			22
13a	*t*-Bu	H	*t*-Bu	H	*t*-Bu	ClO_4	acetonitrile	pol.[b]	-0.980			22

B. Aryl substituted pyrylium salts

14a	Ph	H	H	H	Ph	ClO_4	acetonitrile	pol.[b]	-0.320			22
14a	Ph	H	H	H	Ph	ClO_4	acetonitrile	pol.	-0.230			32
15a[g]	Ar^1	H	H	H	Ar^1	ClO_4	acetonitrile	pol.[b]	-0.500			22
16a[g]	Ar^2	H	H	H	Ar^2	ClO_4	acetonitrile	pol.[b]	-0.680			22
17a	Ph	H	Ph	H	Ph	ClO_4	EtOH	pol.	-0.360	-0.850	24691	15
17a	Ph	H	Ph	H	Ph	ClO_4	DMF	pol.	-0.301			16
17a	Ph	H	Ph	H	Ph	ClO_4	acetonitrile	pol.	-0.280	-1.530		32
17a	Ph	H	Ph	H	Ph	ClO_4	acetonitrile	pol.[b]	-0.490			22
17b	Ph	H	Ph	H	Ph	BF_4	acetonitrile	pol.[c]	-0.696	-1.850		62
17b	Ph	H	Ph	H	Ph	BF_4	acetonitrile	pol.[d]	-0.709	-1.895		62
17b	Ph	H	Ph	H	Ph	BF_4	acetonitrile	pol.[e]	-0.660	-1.820		62
17b	Ph	H	Ph	H	Ph	BF_4	EtOH	pol.	-0.300	-1.840	24691	15
17d	Ph	H	Ph	H	Ph	$AlCl_4$	1M HCl	pol.	-0.300	-0.840	24510	5
17e	Ph	H	Ph	H	Ph	Cl	EtOH	pol.	-0.344	-0.720	25000	15
17f	Ph	H	Ph	H	Ph	Br	EtOH	pol.	-0.304	-1.110	27248	15
17c	Ph	H	Ph	H	Ph	I	EtOH	pol.	-0.220	-1.160	22222	15
17c	Ph	H	Ph	H	Ph	I	DMF	pol.	-0.404			16
17g	Ph	H	Ph	H	Ph	IO_3	EtOH	pol.	-0.850	-0.850	24390	15
17h	Ph	H	Ph	H	Ph	IO_4	EtOH	pol.	-0.215	-0.670	22222	15
18a	Ph	Ph	Ph	H	Ph	ClO_4	acetonitrile	pol.	-0.290	-1.500		32
18b	Ph	Ph	Ph	H	Ph	BF_4	EtOH	pol.	-1.280	-1.980	27174	15
19b	Ph	Ph	H	Ph	Ph	BF_4	EtOH	pol.	-1.010	-1.540	22831	15
20a	Ph	Ph	Ph	Ph	Ph	ClO_4	acetonitrile	pol.	-0.420	-1.560		32
20b	Ph	Ph	Ph	Ph	Ph	BF_4	EtOH	pol.	-1.150	-1.600	23810	15

20f	Ph	Ph	Ph	Ph	Ph	Br	EtOH	pol.	-0.848	-1.440	23810	15
21a[g]	Ph	Ph	Ar^3	Ph	Ph	ClO_4	acetonitrile	pol.	-0.450	-1.630		32
22a[g]	Ar^3	Ph	Ph	Ph	Ar^3	ClO_4	acetonitrile	pol.	-0.430	-1.580		32

C. Alkyl-aryl substituted pyrylium salts

23a	Me	H	Ph	H	Me	ClO_4	1M HCl	pol.	-0.577		30580	5
24a	Me	H	Me	H	Ph	ClO_4	DMF	pol.	-0.530			16
24a	Me	H	Me	H	Ph	ClO_4	1M HCl	pol.	-0.580		28990	5
25a	*i*-Pr	H	Ph	H	*i*-Pr	ClO_4	1M HCl	pol.	-0.566			18
26a	*c*-Pr	H	Ph	H	*c*-Pr	ClO_4	1M HCl	pol.	-0.520			18
27a[g]	*t*-Bu	H	Ar^2	H	*t*-Bu	ClO_4	acetonitrile	pol.[b]	-0.880			22
28c	Me	H	Ph	H	Ph	I	1M HCl	pol.	-0.408		26740	5
28c	Me	H	Ph	H	Ph	I	DMF	pol.	-0.409			16
29d	Ph	H	Me	H	Ph	$AlCl_4$	1M HCl	pol.	-0.394		25510	5
30b	Ph	Me	H	Me	Ph	BF_4	EtOH	pol.	-0.965	-1.440	25510	15
31b	Ph	Et	H	Et	Ph	BF_4	EtOH	pol.	-1.020	-1.580	27248	15
32b	Ph	Me	Ph	H	Ph	BF_4	EtOH	pol.	-0.420	-0.820	27397	15
33b	Ph	Et	Ph	H	Ph	BF_4	EtOH	pol.	-0.955	-1.590	25316	15
34b	Ph	Me	Ph	Me	Ph	BF_4	EtOH	pol.	-0.500	-1.570	27027	15
35b	Ph	Et	Ph	Et	Ph	BF_4	EtOH	pol.	-0.908	-1.440	27248	15

D. Organometallic substituted pyrylium salts

36a	Ph	H	C_5H_4-$Mn(CO)_3$	H	Ph	ClO_4	acetonitrile	pol.	-0.350	-1.230		23
								pol.[f]	-0.350	-1.270		23
37a	*t*-Bu	H	C_5H_4-$Mn(CO)_3$	H	*t*-Bu	ClO_4	acetonitrile	pol.	-0.450			23
								pol.[f]	-0.400			23
38a	*t*-Bu	H	C_5H_4-$Re(CO)_3$	H	*t*-Bu	ClO_4	acetonitrile	pol.	-0.490			23
								pol.[f]	-0.530			23

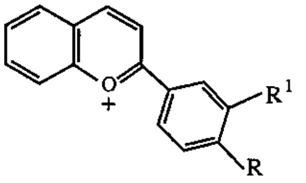
E. Carboranyl derivatives of pyrylium salts

39i	*t*-Bu	H	R	H	*t*-Bu	$SnCl_6/2$	acetonitrile	pol.[b]	-0.180			22
40i	Ph	H	R	H	Ph	$SnCl_6/2$	acetonitrile	pol.[b]	-0.380			22
41i	Ar^1	H	R	H	Ar^1	$SnCl_6/2$	acetonitrile	pol.[b]	-0.100			22

Notes : [a] Letters **a** to **i** indicate the anions of the pyrylium salts; [b] oscillopolarography; [c] integrated d. c. polarography; [d] normal pulse polarography; [e] reverse pulse polarography; [f] cumulation polarography; [g] Ar^1 =*p* -methoxyphenyl; Ar^2 = 3,5-di-*t*-butyl-4-hydroxyphenyl; Ar^3 = *p*-tolyl.

discrepancy between results obtained by different polarographic techniques, under different experimental conditions, and, most disturbing, from different laboratories. In the following discussion more emphasis will be placed on conclusions based on data which are in reasonable agreement with those obtained by most workers. For example, for the 2,4,6-triphenylpyrylium cation there is a preponderence of $E_{1/2}$ values at 0.300 ± 0.080 V, without a systematic variation with anion and solvent. The few results outside this range might be considered questionable.

The behavior in the electrochemical reduction is the same (one-electron reduction of **1** to **2**) for alkyl-, aryl-, and styryl-substituted pyrylium salts,[21] as well as for cations bearing carboranyl[22] and metal-containing ($-C_5H_4M(CO)_3$, where M = Mn or Re) substituents,[22] and for condensed ring systems like **42-45**.[22,24-27]



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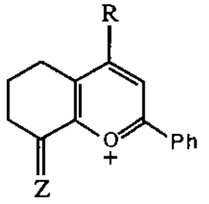
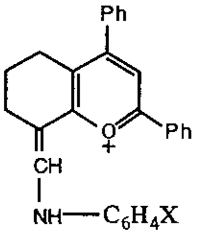


43 $Z=H_2$, R=H
44 Z=CHAr, R=Ph



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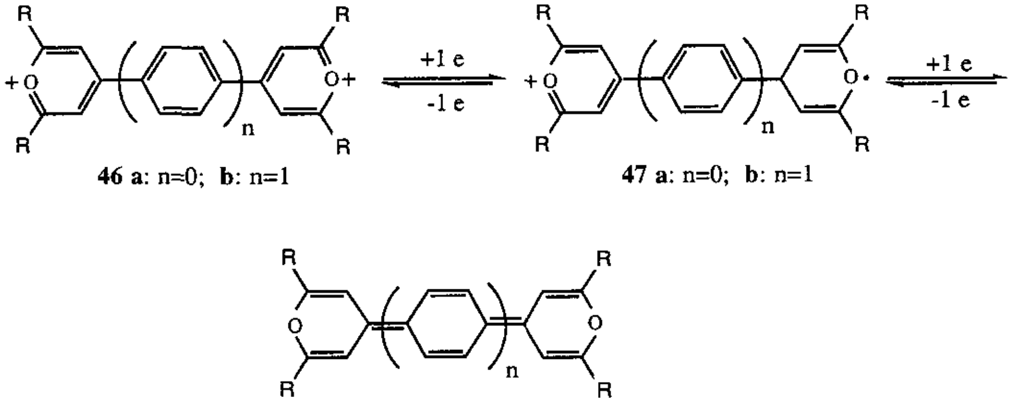
The quantitative effects of substituents upon the reducibility of the ring are far from clear. It was claimed that electron-donating substituents hinder reduction, because $E_{1/2}$ for α and γ phenyl substituted pyrylium and benzopyrylium salts becomes more negative when donor groups are introduced into the phenyl substituents.[19,22,23,28,29] An approximate correlation of $E_{1/2}$ with the Hammett σ constants of X in **45** was reported.[26] It was found, however, that replacement of a methyl substituent in α or γ by the better donor phenyl makes $E_{1/2}$ *less* negative,[5,16,29,30] and replacement of a methyl by cyclopropyl (cf. **10**, **11**, and **26**[17]) has almost no effect.[18] The order of electron donating ability of substituents in pyrylium is Me << Ph<< 2-thienyl < cyclopropyl < *p*-anisyl.[31]

In another study, replacing a γ hydrogen by carboranyl increases $E_{1/2}$ for one structure and lowers it for another.[22] Finally, the electron donating effect of the phenyl groups in 2,4,6-triphenylpyrylium should certainly be stronger than of the severely tilted phenyl groups in pentaphenylpyrylium. Nevertheless, it is the latter that has the more negative $E_{1/2}$ of the two.[32]

Depending upon structure, two pyrylium rings found in the same molecule can be reduced in succession (two one-electron steps) or simmultaneously (one two-electron step). Two steps are observed if the pyrylium moieties are connected by an extended π electron system, because of the stability of the intermediate pyranylpyrylium cation radical.[33-35]



46 a: n=0; **b**: n=1

47 a: n=0; **b**: n=1

48 a: n=0; **b**: n=1

The polarographic reduction of 4,4'-bispyrylium salts (**46a**), of their phenylogues (**46b**) and of the azo analog (-N=N- instead of phenylene) was extensively investigated,[33,34] as was also the polarographic reduction of compounds in which the pyrylium rings are connected by a system of phenylene rings and double bonds.[35] The process has two steps in each case, and the final product has dipyranylidene structure, e.g. **48** (eq. 1). Each step is fully reversible, which proves again the stability of the cation radical (**47**).

By contrast, the oscillopolarograms of dications in which the connecting element contains an "electronic insulator" group (such as CMe_2 or an oxygen atom) display only one two-electron wave, the intermediate cation radical being hardly observable.[22] In this respect bispyrylium cations are similar to bispyridinium and bisimidazolium cations.[33,36,37]

The various polarographic methods give information about reduction potentials, but not about the mechanism of the more complex processes taking place during electrochemical reduction. The electron transfers do have finite rates which are dependent on activation parameters[38-40] and are often preceeded, or followed, or both preceded and followed by chemical reactions.[41-43] To be able to elucidate the mechanism in such cases, the investigations in the field shifted from the static determination of potentials (obtained by polarography) to the dynamic determination of currents, investigated by voltammetry.[44] *Cyclic voltammetry* (CV),[45] (named once *"Electroanalytical Spectroscopy"* [44]) enables one to have a deeper insight into the redox processes because it gives information on :

i) thermodynamic parameters (redox potentials);

ii) kinetics of heterogeneous electron transfer and coupled chemical reactions;

iii) transient intermediates generated electrochemically ;[44,46]

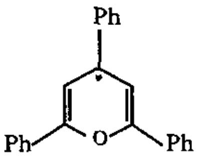
iv) quantitative interpretation of the important parameters in terms of their voltammetric response,[47-54] because the mathematical analysis of the theoretical background was developed and improved by means of numerical methods.[55,56] A good part of the work described in the following sections was posible because of cyclic voltammetry.

Polarography proved to be a useful investigation method of the action mode of pyrylium salts as corrosion inhibitors,[57,58] because the inhibition is related to the adsorption-desorption of the pyrylium cations. The first paper on the subject concluded that adsorption-desorption phenomena of both cations and resulting free radicals are important in the electrochemical reduction of pyrylium salts at low concentration (10^{-5}M).[24,59] Subsequently, a detailed study[60-62] of this adsorption-desorption at the electrode-solvent interface showed no adsorption of the 2,4,6-trimethylpyrylium cation (**6**) and of the corresponding intermediate free radical, both in organic media and in aqueous solutions.[60] The 2,4,6-tri-*t*-butylpyrylium fluoroborate (**13b**) was surface-active in acetonitrile and in aqueous 0.5 M H_2S0_4 solutions.[60] The reduction of 2,4,6-triphenylpyrylium fluoroborate (**17b**) in acetonitrile was investigated in detail by d. c. polarography, normal, and reverse pulse polarography. The a.c.polarograms[61] in aqueous solution showed that the cation was adsorbed at all potentials prior to its reduction and that the free radical generated was also surface-active.

2.2. Chemical reduction

Various chemical reagents have been used to reduce pyrylium cations to free radicals or to bis-(4*H*)-pyranyl compounds.The earliest report used the vanadous ion[1] to convert the 2,4,6-triphenylpyrylium (**17**) to the corresponding free radical (**49**). Considering the respective oxido-reduction potentials many other metal ions and non-nucleophilic compounds with reducing properties should be effective for these conversions, but little work along these lines was conducted afterwards. Likewise, of many metals which can reduce cations (**1**) only a few (Ag, Cu, Mg, but especially Zn) have been investigated.[5,9,63] In particular, reduction with zinc[9] has become the standard method for preparative one-electron reduction, used whenever structural proof is sought.[29, 65-71]

The application of organometallic compounds, like the K salt of cyclooctatetraene or Na diphenylketyl to prepare dimer (**50**) from **6** was reported without any consideration of mechanism.[64] (For Zn reduction, formation of **49** from **17** was shown by its reaction with diphenylpicrylhydrazyl.[9]) Later, it was found that Grignard reagents also can serve as one-electron donors for pyrylium ions.[72]



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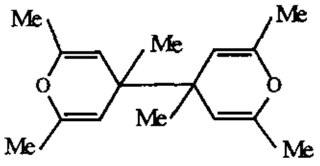

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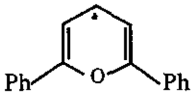

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The first example of pyranyl radical formation by one-electron transfer from a neutral, otherwise stable organic molecule was discovered in the reaction of aryl-substituted pyrylium salts with pyridine.[65] Formation of persistent free radicals was demonstrated in all cases by esr and in the case of reduction of **17** the high resolution esr spectrum showed that the free radical (**49**) is the same as from the reduction of **17** with zinc. It was also shown that the full transfer is preceeded by a charge transfer interaction (see below).[73] The reaction is slow and reversible, and a steady concentration of free radical was maintained even for the unstable 2,6-diphenylpyranyl free radical (**51**), allowing observation of its esr signal. Cations (1) containing "benzylic" CH bonds in α and γ do not form free radicals, but form methylenepyrans by hydron transfer.[74]

Subsequently, the use of other organic bases such as *N,N,N',N'*-tetramethyl-*p*-phenylenediamine[67] and sterically hindered alkoxy[75] and phenoxy anions[67] as one-electron donors to **1** was published. As expected from previous work,[65, 74] only aryl and *t*-butyl can be present as substituents in α and γ. It was also found that the reduction of the same type of cations (**1**) to free radicals can be achieved photochemically, in THF or DME solutions.[70,71] The electron source was considered to be the solvent. In the latter paper it was disclosed that a "reductant ", triphenylphosphine or hexamethylbenzene, was necessary for the reaction to occur.[71] In light of the earlier work using pyridine,[65] it appears likely that the electron donor is the "reductant" rather than the solvent as presumed by the authors.[71]

An electron transfer between two molecules with even number of electrons forms a pair of free radicals or radical cations. In most such reactions involving ions (**1**) examined so far, the pyranyl radical was the only product investigated. An exception was provided by the reaction of the 2,4,6-triphenylpyrylium cation (**17**) with anions $TpM(CO)_3^-$, where Tp is hydrido-tris-(3,5-dimethylpyrazolyl)borate and M is Mo, W, and Cr (**52**, eq. 2).[76]

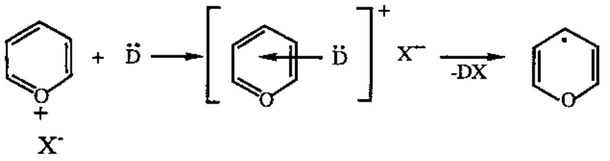
$$\underset{\mathbf{52}}{TpM(CO)_3^-} + \underset{\mathbf{17}}{Ph_3\pi^+} \rightleftharpoons \underset{\mathbf{53}}{Tp\dot{M}(CO)_3} + \underset{\mathbf{49}}{Ph_3\pi^\bullet} \qquad (2)$$

Both odd-electron species (2 and 53) were identified qualitatively and measured quantitatively. The electron transfer was reversible and the equilibrium constant was determined. It varied with the metal (Mo <W < Cr), with the substituents in **1** (triphenylpyrylium >2,4,6-trianisylpyrylium), with the degree of dimerization of **2** to **3**, and with the degree of pairing of reactants in tight ion pairs.[76]

The esr spectra of both odd-electron products were also observed in the reaction of **17** with *N,N,N′,N′*-tetramethyl-*p*-phenylenediamine.[67]

2.3. Charge-transfer complexes

Pyrylium cations (**1**) give rise to short range interactions with electron donors (**54**) in charge-transfer (CT) complexes (**55**), upon which the cations are transformed to less polar electronically excited states (eq. 3).



1 **54** **55** **2**

(3)

In some cases the anion of the pyrylium salt itself (X = I , SCN , SeCN , Br) acts as the donor in CT salts, leading to additional absorption bands in the uv spectra (CT bands, having λ_{max}=400-560nm),[13,77-80] and the fluorescence is quenched. The donor ability of the anions increases in the order $Br^- < SCN^- < SeCN^- < I^-$; as expected from the ionization potentials of the anions.[79]

CT complexes may undergo further transformation to pyranyl radicals (**2**), as demonstrated in the reaction of arylpyryliums with pyridine. It was proposed that the donor-acceptor complex is excited thermally to a low-lying triplet state, which then dissociates to **2** and the pyridine cation radical.[65]

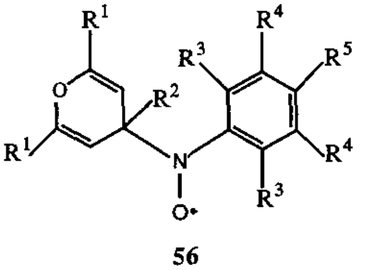
Spectroscopic studies of charge transfer complexes with aromatic amines, anthracene, and phenothiazine were published. A linear correlation was found for : i) the CT absorption bands of the 2,4,6-triphenylthiapyrylium cation *vs*. the $E_{1/2}$ oxidation potential of different donors; ii) the CT absorption bands of anthracene with different substituted pyrylium salts *vs.* the $E_{1/2}$ reduction potential of the corresponding cations.[81]

An investigation of seven pyrylium cations with a range of donors led to the conclusion that two complexes, one in the ground state and a different one in the excited state, were formed in certain cases.[82]

2.4. Properties of pyranyl radicals

This section is concerned mainly with dimerization and esr spectra of free radicals (**2**). Their one-electron reductions and oxidations are discussed in separate sections.

Dimerization. Product isolation in the first studies of electrochemical[9] and chemical[9,63] reductions of **6** gave directly the dimer (**50**). Chemical trapping of the 2,4,6-trimethylpyranyl radical was achieved only recently, with derivatives of nitrosobenzene; the nitroxyl free radicals thus formed (**56**) were identified by their esr spectra.[30] The 2,6-diphenylpyranyl radical (**51**), which also dimerizes fully, was likewise trapped.[30] Photochemical reduction of the parent 2,6-diphenylpyrylium (**14**) in flash photolytic experiments allowed the dimerization rate of **51** (k=1.2 x 10^9 l mol^{-1} sec^{-1}) to be measured.[70] A similar value for this rate was obtained by nanosecond time-resolved cyclic voltammetry.[83] By contrast, reaction of **14** in pyridine gave a steady concentration of **51** which could be analyzed by esr.[65]



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A 2,4,6-trisubstituted pyranyl free radical (**2**) exists in equilibrium with its dimer if at least two of the substituents are aryl groups.[29] Dimerization of **2**, $R^2 = R^4 = R^6 = t$-Bu, $R^3 = R^5 = H$ (**57**) is sterically inhibited.[68] Dimerization is also precluded in strongly acidic solution by the hydronation of the free radical (**2**), which acts as a base. This reaction will be discussed in more detail in Section 3.2.

The position of the dimerization equilibria of a number of pyranyl radicals was determined by esr[29] and by uv-visible spectrocopy.[71] but the results are in poor agreement: the dimerization enthalpies reported for **49** were -10 [71a] and -16 kcal/mol,[29] whereas for the pentaphenyl analog, the values were +2.4,[71b] and -6.0 kcal/mol.[29] At room temperature, the tri- (**49**),[29,84] tetra-[29] and pentaphenyl derivatives[29] were found to be entirely in the free radical forms, with no measurable **3** present. It was also stated that an activation barrier of 6.4 kcal/mol exists for the recombination of **49**.[84] It is not clear, however, how this value was derived, because no rate measurements, but only equilibrium measurements were reported.[84]

The electrochemical behavior of cations (**1**) has allowed an estimation of the rates of dimerization. Three classes of compounds were distinguished:[85]

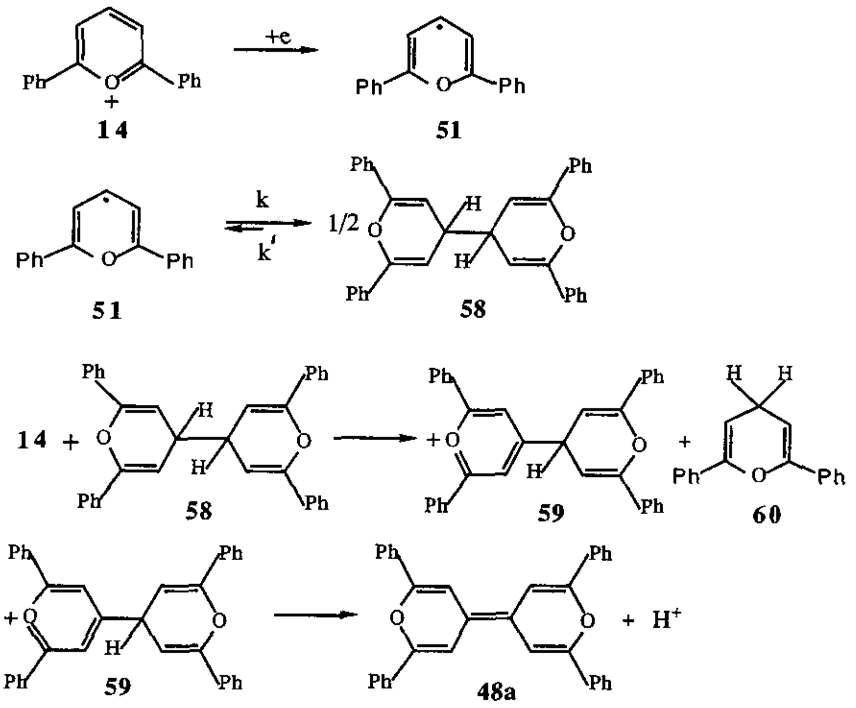
(1) For cations (**1**) with an unsubstituted 4 position , or substituted with methyl or benzyl, dimerization of radicals (**2**) is too fast to be measured.

(2) For 2,4-diaryl-6-methyl- or -6-styrylpyrylium salt, dimerization of **2** occurs with a rate constant of 10^3 to 10^4 l mol^{-1} sec^{-1} and it is essentially complete.

(3) For 2,4,6-triarylsubstituted cations, dimerization is only partial. Further substitution of **1**, at C-3 and C-5, increases the amount of dimer at equilibrium.

The structure of dimers was usually assumed to be **3a**. Bonding at C-4 of one pyranyl with the *para*-position of the γ-phenyl of the other was also proposed without proof for the dimer of **49**.[71b] Some irregularities in the electrode reactions of the mixture of **49** and its dimer were interpreted to mean that the 4,4' dimer is the kinetically controlled product and that it transposes slowly to the 2,2' or 2,4' dimer, which is more stable by 5.8 kcal/mol.[85] In another study, electrolysis of **17** at -1.200 V gave a mixture consisting of three or four products, which could not be separated.[62]

Reduction of 2,6-diphenylpyrylium (**14**) to the unstable free radical (**51**) should lead to the dimer of the latter (**58**).[86] This simple pathway is followed only in very dilute solutions (10^{-3} M). Under usual conditions (reduction with zinc in MeCN) the dipyranylidene (**48a**), resulting from a hydride transfer from **58** to **14**, is isolated in preparative yield (eq. 4 - 7).[69] The same mechanism applies in the electrochemical reduction of **14**.[87] It had been known that pyrylium salts can act as hydride acceptors.[88] A mechanism consisting of a hydrogen atom transfer from **58** to **51** followed by oxidation to **48a** was considered and rejected.[89]



(4)

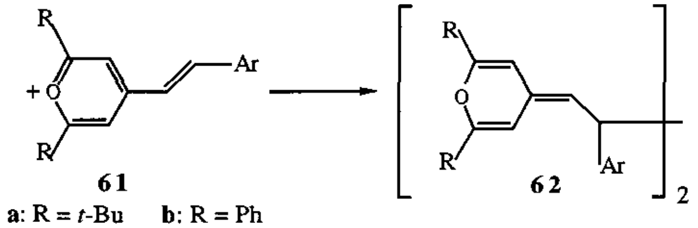
(5)

(6)

(7)

Bispyranylidenes are also prepared by electrochemical[90] and photochemical[91] coupling of pyranthiones.

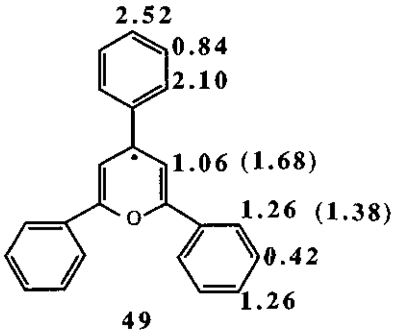
An unusual reaction pattern was observed in the cyclic voltammetry of α- and γ-styrylpyrylium salts (e.g. **61**). The free radicals dimerized in the side chain and gave bis(pyranylidene)ethanes (**62**, eq. 8). In acidic medium compounds (**62**) are converted into bispyrylium salts. The reduction of the latter gives di-spiro compounds.[21]



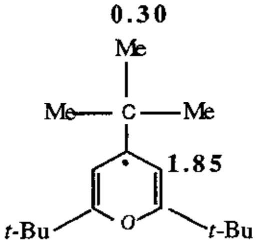
a: R = *t*-Bu b: R = Ph

(8)

Esr Spectroscopy. The first esr spectrum reported for **49** consisted of an unresolved signal.[63] The fully resolved spectrum was published and interpreted a few years later.[92] The hyperfine coupling constants (hfc-s), in Gauss, for protons are shown on the structure below. Based on these, it was concluded that the highest unpaired spin density is present in the γ position. A more recent work revised two of the hfc-s. The new values are shown in parantheses.[71a] It is noteworthy that the analogous phosphabenzene cation radical (**49**, P^+ instead of O) gives an identical splitting pattern for its half-signal.[93] The hfc-s for 2,4,6-tri-*t*-butylpyranyl (**57**) show that more unpaired spin density is present in the central ring than for **49**, as expected.[68]



49



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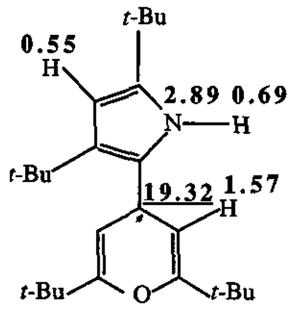
The hfc-s of **2** containing γ-pyrrolyl susbstituents perpendicular to the pyranyl ring (**63** and **64** to be contrasted with **65**) indicated the existence of C - N hyperconjugation. In addition to proton hfc-s, formulae (**63** - **65**) show the carbon hfc-s (underlined).

It should be noted that all resolved esr spectra of **2** were obtained for radicals generated by chemical reduction, with zinc[68,71,92,93] or organic donors.[65,67]



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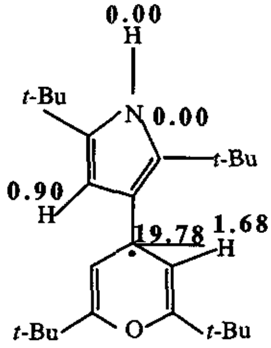

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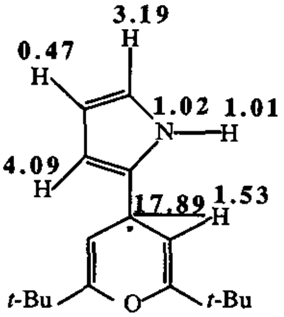


65

As mentioned above, the intensity of esr signals was used to calculate dimerization equilibrium constants.[29] It was also observed that signals for radicals (**2**) generated in pyridine solution have different intensities for different precursors : **14** < **18** < **20** - **22** < **17**.[65] This sequence may reflect a combination of the electron transfer and dimerization equilibria.

3. REOXIDATION OF PYRANYL RADICALS TO PYRYLIUM CATIONS

3.1. Electrochemical oxidation

It was shown by cyclic voltammetry in MeCN that the triphenylpyranyl radical (**49**) is obtained from **17** at -0.320V and reverts to the latter at -0.200V.[28] Measurements of collection efficiency in the voltammetry of **17** on a rotating disk electrode showed that the extent of reoxidation is a function of the rate and equilibrium of dimerization of **49**.[85] In oscillopolarography the dissociation of the dimer was the rate-determining step for reoxidation to **17**.[85]

Dipyranylidenes (**48**) are reoxidized to bispyrylium dications (**46**). Just as for reduction of **46** (Section 2.1.), oxidation occurs in two one-electron steps whenever the unpaired electron in the intermediate cation radical (**47**) is delocalized over both rings, otherwise the one-step two-electron oxidation prevails.[22,33-35,95] The observation of one two-electron oxidation wave for the benzo- and dibenzo-derivatives of **48** [95] most probably reflects the twisting of the bond connecting the two pyranyl rings. Bis(pyranylidene)ethanes (**62**) are oxidized in one two-electron step and form 1,2-bis(pyrylium)cyclobutanes.[91]

The bispyrans (**3**) can be oxidized without prior dissociation (eq. 9), at voltages higher than required for radicals (**2**), as first demonstrated for hexamethylbispyran (**50**). The product was identified as **6**.[9] Oxidation of the hexaphenyl analog was shown later to follow the same pathway.[28,85,87]

$$\pi_2 \xrightarrow{-e} \pi_2^{\cdot +} \longrightarrow \pi^{+} + \pi^{\cdot} \xrightarrow{-e} 2\,\pi^{+} \qquad (9)$$

Oxidation of 1,5-pentanediones and 3,5-pentadien-1-ones on a rotating platinum electrode also led to pyrylium cations (**1**).[96]

3.2. Chemical oxidation

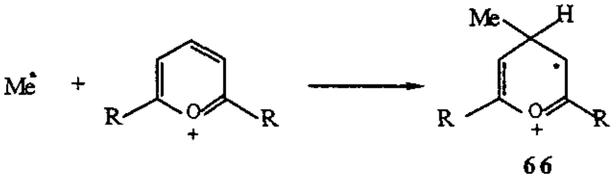
As expected from the oxido-reduction potentials, free radicals (**2**) are easily oxidized to cations (**1**). The first reported example was oxidation of **49** by ferric chloride.[1] Oxidizing agents as uncommon as phenyldiazonium ions or carbon tetrachloride (eq. 10) have been employed.[84]

$$\underset{\mathbf{49}}{Ph_3\pi^{\bullet}} + CCl_4 \rightleftharpoons \underset{\mathbf{17e}}{Ph_3\pi^{+}Cl^{-}} + {\bullet}CCl_3\,\text{(dimerizes)} \qquad (10)$$

Oxidation of pyranyl free radicals with Fe^{+3} most probably intervenes in the conversion of 2,6-diphenyl- (**14**) and 2,6-di-tert-butylpyrylium (***12***) *to the corresponding 4-methyl homologs in the presence of t*-butyl hydroperoxide (eq. 11-13). The process also involves combination of the pyrylium cation with a (nucleophilic) methyl free radical.[97]

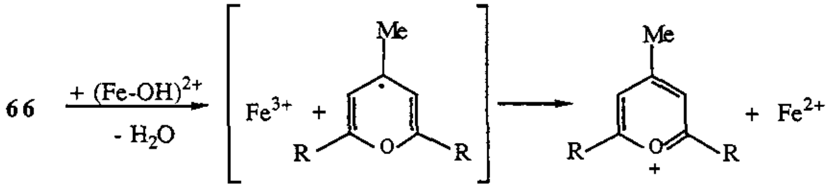
Larger alkyl groups (R) were likewise introduced by reaction with carboxylic acids (RCOOH), peroxydisulfate as oxidizing agent, and a silver salt as catalyst.[98]

$$t\text{-BuOOH} + \text{Fe}^{2+} \longrightarrow \text{M}\dot{\text{e}} + \text{Me}_2\text{CO} + (\text{Fe-OH})^{2+} \qquad (11)$$



66

(12)



(13)

The same type of intermediate as **66** was formed by hydronation of the pyranyl free radical when the electrochemical reduction of **1** was conducted in strongly acidic solutions. A second electron transfer converts **66** into the 4*H*-pyran.[25,84,99] In the acid solution the latter reacts as a 1,5-pentanedione.[100]

It was proposed that hydride abstraction from 4*H*-pyrans also consists of an electron transfer giving a cation radical such as **66**, followed by loss of a hydron and a second electron transfer.[23,101]

Oxidation of pyranyl radicals (e.g. **49**) with cation radicals of polycyclic aromatics (most usually rubrene, Rr) generated electrochemically leads to the excited state of the latter, the decay of which produces chemoluminiscenece (eq. 14-16).[28,102] Non-dissociated bispyrans (e.g. **58**) are also oxidized (eq. 17) to their cation radicals, which then cleave rapidly according to eq. 9, and another quantum of light is emmited by the reaction sequence of eqs. 14 - 16.[102]

$$\text{Rr}^{\bullet+} + \pi^{\bullet} \longrightarrow {}^{3}\text{Rr}^{*} + \pi^{+} \qquad (14)$$

$$2\ {}^{3}\text{Rr}^{*} \longrightarrow {}^{1}\text{Rr}^{*} + \text{Rr} \qquad (15)$$

$$^{1}\text{Rr}^{*} \longrightarrow \text{Rr} + h\nu \qquad (16)$$

$$\text{Rr}^{\overset{+}{\bullet}} + \pi_2 \longrightarrow {}^{3}\text{Rr}^{*} + \pi_2^{\bullet+} \qquad (17)$$

The hexamethylbispyran (**50**) was oxidized to **6** by chromium trioxide in perchloric acid.[9]

Reaction of tetraphenylbispyran (**58**) with triphenylmethyl cations gave the bispyrylium (**46a**) in high yield (reverse of eq. 1).[67] Esr measurements showed that the cation radical (**47a**) was present in the mixture. It was proposed that **47a** was the intermediate, formed by one-electron transfer from **58** and loss of a hydrogen molecule.[67] This mechanism is contradicted by the report that the molecular ion of **58** generated chemically or electrochemically does not lose H_2, but instead it dissociates as in eq. 9.[102] It is thus possible that **47a** was only a by-product (the absolute intensity of the esr signal was not measured[67]). Its formation can be explained by a small extent of electron transfer to **58** followed by cleavage to the pyranyl radical (**51**) and the pyrylium ion (**14**), which would react with another molecule of **58** to form **47a** and the 4*H*-pyran (**60**).

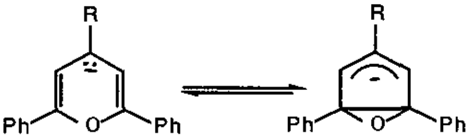
4. TWO-ELECTRON TRANSFERS TO PYRYLIUM SALTS. PYRANYL ANIONS

Following the observation of pyranyl free radicals in the solutions of pyrylium perchlorates in pyridine,[65] a polarographic investigation of several perchlorates (**1**) in anhydrous acetonitrile was conducted in the same laboratory.[32] It was found that the cations which had formed stable pyranyl radicals in the former study[65] exhibited a second reduction wave at -1.500 to -1.630 V. By contrast, salts (**6a**) and (**14a**), which gave pyranyl radicals that dimerized fully, did not show a second reduction wave in the polarogram. It was concluded, therefore, that the second reduction involved the free radicals and gave pyranyl anions.[32] Inasmuch as the reduction potentials of some of the cations (**1**) studied there were never disclosed in the literature, they are included in Table 1.

An extensive study of 25 perchlorates (**1**) in acetonitrile, using voltammetry and oscillopolarography at a rotating disc electrode, cyclic voltammetry, and coulometry of the potentiostatic reduction, demonstrated unambigously that the conversions **1** → **2** → **4** of Scheme 1 do occur.[85] It was also found that dimerization of **2** to bispyrans decisively influences the voltammetric behavior.[85] In reductions of cations (**1**) at -1.500 V or lower, coupling of anions (**4**) with cations (**1**) takes place as well.[62]

When the catodic reduction of 2,4,6-triarylpyrylium perchlorates at the voltage of the second step was conducted in the presence of a large excess (10 : 1 to 1000 : 1) of an alkyl halide, alkylation of the pyranyl anions (**4**) took place.[103] The 4-alkyl-2,4,6-triaryl-4*H*-pyrans were isolated in 11 - 36% yield. The reaction rates of various alkyl halides with the anion from **17** were determined and found to follow the normal order of S_N2 reactions.[103]

The pyranyl anions derived from **14** (**67a**) and **17** (**67b**) were obtained from the corresponding 4*H*-pyrans and very strong bases.[104] For the 2,4,6-triphenyl-4*H*-pyran a pK_a value of 37 ± 2 was estimated. As expected for six-membered rings with 8 π electrons, anions **67** react in the bicyclic form **68**.[104,105]

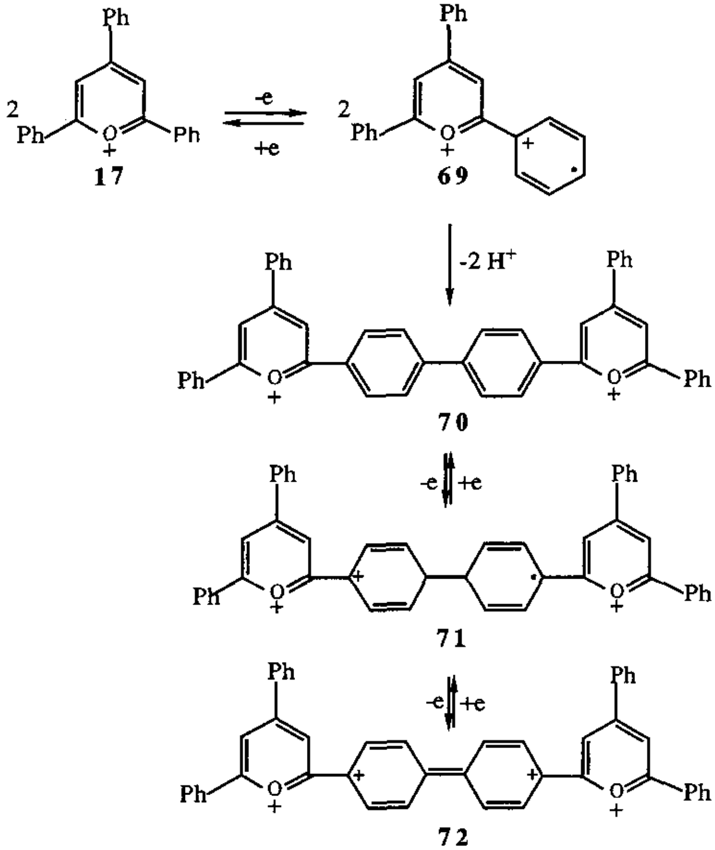


67 a: R = H **68**
b: R = Ph

5. ONE-ELECTRON OXIDATION OF PYRYLIUM CATIONS

The anodic oxidation of pyrylium, benzopyrylium, and thiapyrylium cations as well as of a large number of pyridinium and imidazolium salts was investigated[106] by cyclic voltammetry in 0.1M CF_3COOH / HSO_3F at -76°C. Almost all cations were oxidized to relatively stable dication radicals. The oxidation potentials decrease with decreasing acceptor ability of the heterocyclic ring, increasing size of the π-electron system, and increasing donor properties of substituents. The voltammograms of 2,4,6-trialkylpyrylium heterocycles exhibit a single one-electron oxidation wave at $E_{1/2} = +2.050 \pm 0.020$ V (for 2,4,6-trimethyl- and 2,6-di-*t*-butylpyrylium cations) which indicates the formation of the pyrylium dications of type **5**. Alkylaryl- and arylpyrylium cations which contain more extended π-electron systems exhibit a different behavior, as shown in Scheme 2 for the example of triphenylpyrylium (**17**). For these, the polarograms consist of two or more one-electron oxidation waves. The first oxidation occurs at lower potentials than for the trialkylpyrylium cations ($E_{1/2}$ = +1.340 V) and leads to the formation of the dication radicals (**69**). Because the polarograms display typical marks of dimerization, the conversion to the bispyrylium dication (**70**) was postulated.

Scheme 2. The electrochemical oxidation of 2,4,6-triphenylpyrylium salts.



This would mean that in dication radical (**69**), unlike in the free radical (**49**), the unpaired spin density is the highest in the α position. As this dimer (**70**) possesses an even more extended π-electron system than the starting pyrylium salt (**17**), a second electron is removed by oxidation at potentials from +0.790 V to +0.930 V, when radical trications (**71**) are said to be generated. These are further oxidized to tetracations (**72**). The highly charged species (**71**) and (**72**) are presumably stable in the superacidic media in which the oxidations were carried out. When the *para* position of the phenyl substituent bears a substituent (e.g. 2,4,6-tri-*p*-tolylpyrylium cation (**73**) eq. 18), which hinders the dimerization of the intermediate dication radical (**74**), a second oxidation wave is also detected, but in this case the pyrylium trication (**75**) is assumed to be formed.

$$\underset{\mathbf{73}}{\mathrm{Tol}_3\pi^{+}} \underset{+e}{\overset{-e}{\rightleftharpoons}} \underset{\mathbf{74}}{\mathrm{Tol}_3\pi^{+2}} \underset{+e}{\overset{-e}{\rightleftharpoons}} \underset{\mathbf{75}}{\mathrm{Tol}_3\pi^{+3}} \qquad (18)$$

It might be expected that the radical dications formed from 2,6-diphenylpyrylium (**14**) dimerize to give the known **46a**. No indication about further reactions of the radical dications from **14** or **12** is given by the authors.[106]

6. REACTIVITY OF CHALCOGENAPYRYLIUM CATIONS IN ONE-ELECTRON TRANSFER REACTIONS

The chalcogenapyrylium cations (Scheme 1, in which O is replaced by S, Se, Te) form discrete cation/ dication radical, cation/radical, and radical/anion redox systems, a feature which makes them suitable for comparing the effects of chalcogen atoms on electrochemical properties of these six-membered heterocycles. The one-electron polarographic reductions (first step) of pyrylium, thiapyrylium, and selenapyrylium salts were studied under identical experimental conditions and the results were compared with those obtained for the iso-6π-electronic seven- and five-membered aromatic ions.[107] All cations were reduced to the corresponding free radicals, which dimerized. Table 2 presents the first half-wave reduction potentials at the dropping mercury electrode ($E_{1/2}$) and the rotating platinum disc electrode ($E'_{1/2}$) in DMF.

A comparison of some more complex structures was conducted for all oxido-reduction levels.[20] The order of variation was:

a) Cation to free radical, $E_{1/2}$ more negative : Te < Se < S < O;

b) Cation to dication radical, $E_{1/2}$ more positive : Te < Se < S < O;

c) Free radical to anion, $E_{1/2}$ more negative : Te < Se < S < O;

The results show an interplay of π delocalization (Te < Se < S < O) and electronegativity (Te < Se < S < O), in which the former is predominant.[20]

Table 2. The first half reduction potentials (in V) of chalcogenapyrylium cations related to **1** (R^3=R^5=H) obtained by polarography ($E_{1/2}$) and cyclic voltammetry ($E'_{1/2}$) in DMF.

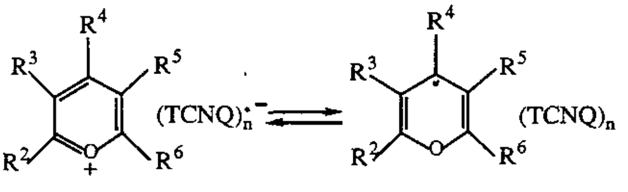
Heteroatom			**O**		**S**		**Se**	
R^2	**R^4**	**R^6**	$E_{1/2}$	$E'_{1/2}$	$E_{1/2}$	$E'_{1/2}$	$E_{1/2}$	$E'_{1/2}$
Ph	H	Ph	-0.32	-0.34	-0.31	-0.33	-0.30	-0.32
Ph	Ph	Ph	-0.37	-0.39	-0.35	-0.37	-0.32	-0.35

7. APPLICATIONS OF ONE-ELECTRON TRANSFER REACTIONS OF PYRYLIUM SALTS

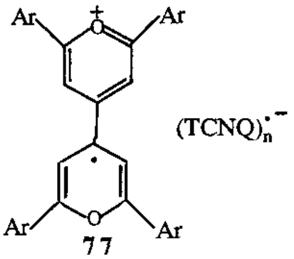
Applications of pyrylium salts have been reviewed.[8] In this section we present some examples meant to complement what was presented in earlier surveys.

A synthetic application, alkylation of γ unsubstituted pyrylium salts by alkyl free radicals,[97,98] was discussed in Section 3. Along a different line, cation (**17**) was used as an electron transfer catalyst in the photoinduced Diels-Alder reaction of indole with substituted cyclohexadienes.[108]

A significant degree of interest was manifested for pyrylium salts which might possess electrical conductivity. For this purpose, salts of tetracyanoquinodimethane (TCNQ) anion radical with pyrylium cations (**76**) were synthetized by two different methods.[109,110] The conductivities of salts (**76**) increase with the increase in the polarity of the cations,[109] but are situated between those of insulators and semiconductors.[110] Their esr spectra showed that the unpaired spin density is concentrated mainly with the anion.[110] It was shown for triphenylpyrylium tetracyanopropenide that the charge transfer between the anion and the cation has less influence on the crystal structure than the electrostatic force or the hydrogen bonding between two anions.[111]



76a **76b**



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A second class of materials studied were the complexes of 4,4'-bispyranylidenes (**48a**) with TCNQ, (**77**). These complexes are better described as ion radical pairs,[76] and exhibit electrical conductivity.[69,112]

Compounds (**77**) in which each aryl group carries at least one long, flexible substituent are liquid-crystalline semiconductors.[113] Interestingly, for obtaining compounds of this class in which each phenyl group bears two alkoxy substituents, reduction of 2,6-diarylpyrylium salts with zinc fails, and electrochemical coupling[89a,90] or photochemical synthesis from thiopyrones[91] have to be used.

ACKNOWLEDGMENT

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