

Electrochemical Oxidation of Aryl Cycloheptatrienes

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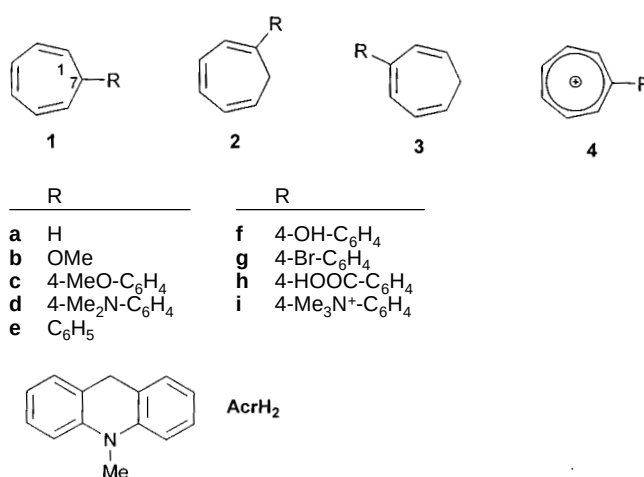
Abstract. The electrochemical oxidation of various substituted aryl cycloheptatrienes and cyclohepta-1,3,5-triene, the parent compound, in acetonitrile is investigated with the aid of cyclic voltammetry (CV), experiments at the rotating ring disk electrode (RRDE) and controlled potential electrolysis. 1-(*p*-methoxyphenyl)-cycloheptatriene **2c**, 1- and 3-(*p*-dimethylaminophenyl)-cycloheptatriene **2d**, **3d** are converted by anodic oxidation into the radical cations the main reaction of which is not the deprotonation. According to the pro-

posed mechanism the electrochemical oxidation proceeds along the radical cation dimerization. The dimer cations (1_2^{2+}) decompose under deprotonation into tropylium ions **4** and starting compound. In the case of 1-(*p*-dimethylaminophenyl)-cycloheptatriene **2d** the deprotonation reaction can compete with the dimerization. The oxidation of the cycloheptatriene compounds is kinetically controlled by the homogeneous chemical steps rather than by the initial electron transfer.

The electrochemical oxidation of hydrocarbons proceeds *via* the radical cation the carbon–hydrogen bonds of which are considerably acid. Generally, the deprotonation of such radical cations plays an important role [1]. In contrast to the cycloheptatriene/tropylium couple [2], redox systems, which can serve as heterocyclic co-enzyme analogues such as the acridan/acridinium couple and dihydropyridine/pyridinium systems were intensively studied [3]. The electrochemical generation of aryltropylium ions from arylcycloheptatrienes is of special interest because various molecular properties such as shape, colour and electron acceptor strength differ strongly from those of tropylium cations. Accordingly, the properties of macrocycles [4] and supramolecular systems such as rotaxanes and catenanes containing cycloheptatriene building blocks [5] are expected to undergo significant changes in response to the loss of electrons.

As part of our research program concerning the photochemical generation of tropylium cations [6] the electrochemical oxidation was carried out to learn about the behaviour of radical cations produced in the absence of any electron acceptor. For this purpose experiments with cycloheptatrienes **1**, **2** and **3** containing aryl substituents of different donor strength and 1,3,5-cycloheptatriene **1a** and the methoxy substituted derivative **1b** were performed. The compounds **1f** – **1i** were only used to evaluate the influence of the substituents on the oxidation peak potentials (see Fig. 1).

Compounds **1d** – **3d** differ from the other cycloheptatrienes studied in their basic properties. This may be meaningful regarding the deprotonation of the related radical cations.



For the sake of comparison under our conditions the redox couple 9,10-dihydro-10-methylacridine (AcrH₂)/10-methyl-acridinium (AcrH⁺) was included.

Results

Cyclic Voltammetry

Peak Potentials

Oxidation and reduction potentials of the isomers **1**, **2** and **3** were investigated by cyclic voltammetric measurements. The peak potentials are compiled in Table 1, which also contains the reduction peak potentials of the corresponding tropylium ions **4**. Interestingly, the peak potential of compound **1b** is much higher than that of

the unsubstituted compound **1a**. This can be explained by the different conformations of the seven-membered ring in these two compounds [7]. Semiempirical calculations (PM3) have shown that the HOMO-energy of compound **1b** is lower (−9.11 eV) than that of **1a** (−8.95 eV).

Table 1 Electrochemical data ^{a)} of cycloheptatrienes (E_p^a) and selected tropylium cations (E_p^c)

Compound	E_p^a /V(SCE)	i_p /μA (F/mol ^{−1})	E_p^c /V (SCE)
1a	1.43	10.8 (1.6)	−0.32
1b	1.78	8.7 (1.3)	—
1c	1.23	6.4 (0.96)	−0.40
2c	1.11	6.2 (0.93)	—
3c	1.20	7.9 (1.18)	—
1d	0.60	7.1 (1.06)	−0.52
2d	0.52	7.2 (1.07)	—
3d	0.55	6.8 (1.01)	—
1e	1.36	7.0 (1.04)	−0.38
1f	1.19	7.5 (1.12)	—
1g	1.41	7.1 (1.06)	—
1h	1.54	5.1 (0.76)	—
1i	1.80	7.1 (1.06)	—

^{a)} peak potentials and the peak currents (i_p) were measured in acetonitrile solution (10^{−3} M) calibrated vs. the ferrocene/ferrocenium couple (0.31 V, 6.7 μA = 1 F mol^{−1})

A priori, **1c–1i** contain two electroactive groups, the aryl and the cycloheptatrienyl moiety. A comparison of the oxidation potentials of **1c** (1.2 V) with that of 4-methylanisole (1.5 V) and **1a** (1.4 V) indicates that the oxidation of **1c** cannot be attributed to separated electrophores. A different situation is encountered in the cases of the cycloheptatriene **1d**. Here, the *N,N*-dimethyl aniline moiety is oxidised. Semiempirical calculations (PM3) of **1e**, **1c** and **1d** indicate that the HOMO of the first compound is localised within the seven-membered ring, distributed between the aryl substituent and the cycloheptatriene ring in **1c**, and localised in the *p*-dimethylaminophenyl residue of **1d**. The exceptional

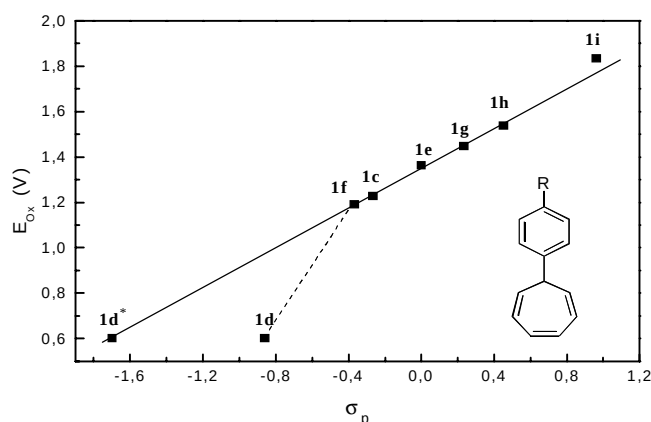


Fig. 1 Plot of the oxidation peak potentials (cyclic voltammograms measured in 10^{−3} M acetonitrile solution) of substituted phenylcycloheptatrienes vs. the σ_p -constants of the substituents (**1d***: σ_p^+ -substituent constant used).

position of **1d** is substantiated by the plot of the oxidation peak potentials of various substituted phenyl cycloheptatrienes vs. the substituent properties (σ_p -values) which is shown in Fig. 1. Because the amino group is primarily oxidised in the case of **1d** the σ_p^+ -substituent constant has to be used in this case.

Notably, the oxidation peak potential of compounds **c** and **e** is much larger than the oxidation potentials of the isomers **d**. The latter do not differ very much from each other and lie around 0.6 V, a value close to that of the oxidation potential of 4-*N,N*-dimethylaminotoluene.

The cyclic voltammograms of **1a**, **2c**, **1d**, **2d**, **4d** and of 4-*N,N*-dimethylamino toluene, the model compound for compounds **d**, recorded at the scan rate 1 V/s are shown in Fig. 2(a)–(d), respectively.

Apart from the first anodic peak the cyclic voltammograms presented in Fig. 2 possess one or several cathodic peaks. The peak heights of the latter are remarkably lower than the anodic peak height.

The cyclic voltammograms recorded both with **1a**, **2c**, **1d** and the other arylcycloheptatrienes indicate that the electrochemical oxidation of these compounds is chemically irreversible. By contrast the cyclic voltammogram of **2d** approaches a quasi-reversible behaviour, a feature becoming even more evident by increasing the scan rate up to 10 V/s. Typical results are presented in Fig. 2e where cyclic voltammograms recorded with compound **2d** at various scan rates are shown.

Irreversibility observed in most cases implies that here the products formed primarily at the electrode surface undergo fast consecutive reactions. Reversibility observed in the case of **2d**, on the other hand, indicates that the oxidation product of **2d**, i.e. the radical cation, must be rather long-lived, i.e. the lifetime must be much longer than that of the radical cations formed in the cases of the isomers **1d** and **3d**. Whereas the cyclic voltammograms of **1d**, **2d** and **3d** exhibit chemical irreversibility of the oxidation process that of *N,N*-dimethyl-*p*-toluidine (E_p^a = 0.6 V), the model substance, demonstrates reversibility. Therefore, it can be concluded that the observed irreversibility is due to the cycloheptatriene ring.

According to Geske [2] the electrolysis of cyclohepta-1,3,5-triene, the parent of the compound **1** family, results in the formation of the tropylium ion. The proposed mechanism assumes two oxidation steps. In the first one the starting compound is converted into a radical cation which readily releases a proton thus forming the cycloheptatrienyl radical which has a lower oxidation potential, and is readily oxidised at the anode (ECE-mechanism).

In the case of the compound AcrH₂ which is similar to cycloheptatriene the deprotonation of the radical cation is clearly indicated. The cyclic voltammogram of AcrH₂ is depicted in Fig. 3.

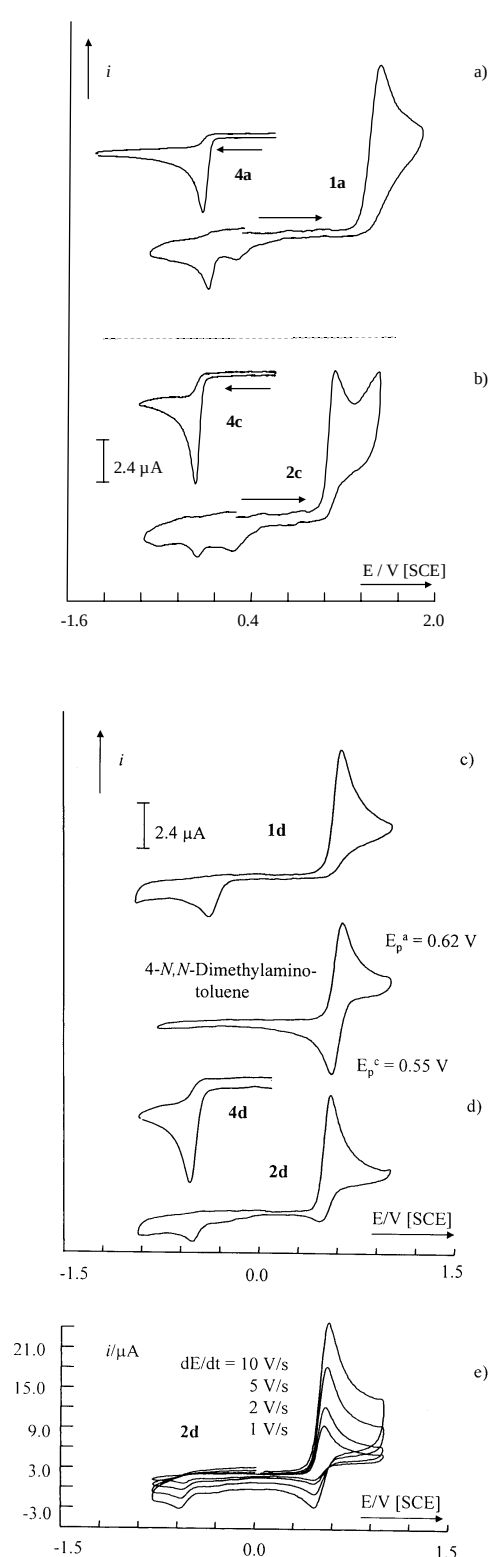


Fig. 2 Cyclic voltammograms recorded in 0.1M Bu₄NPF₆-CH₃CN solution.

a) Compounds **1a** and **4a**, b) compounds **2c** and **4c**, c) compound **1d**, d) compounds **2d**, **4d** and 4-(*N,N*-dimethylamino)-toluene; concentration: 1.0×10^{-3} M, scan rate: 1 V s^{-1} platinum disk electrode (1 mm diameter). e): **2d** at various scan rates.

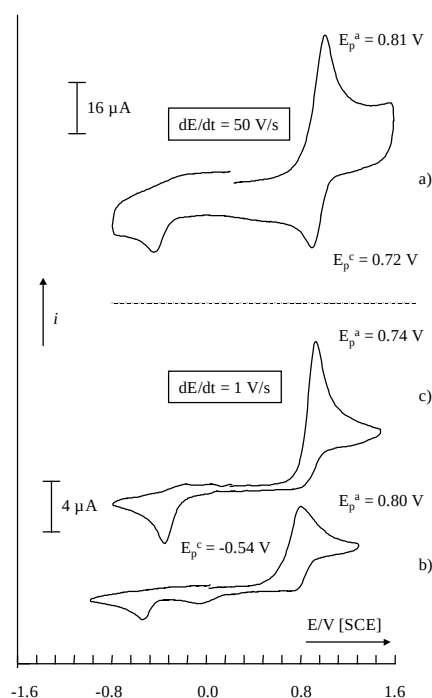


Fig. 3 Cyclic voltammograms of AcrH₂ (platinum disk electrode (1 mm diameter)) recorded in 0.1M Bu₄NPF₆-CH₃CN solution; concentration: 1.0×10^{-3} M. a) scan rate 50 V s^{-1} ; b) scan rate 1 V s^{-1} ; c) addition of 10^{-3} M pyridine.

The oxidation peak at 0.8 V approaches a chemically reversible behaviour under our conditions (carefully dried acetonitrile) even at the relatively low scan rate of 50 V/s . An analogous behaviour was observed by Fukuzumi *et al.* only at 2000 V/s [8].

The peak height of the wave at 1 V/s scan rate demonstrating chemical irreversibility corresponds to 1 F/mol according to the ferrocene/ferrocenium couple. This finding can be explained by assuming the deprotonation of the radical cation AcrH₂^{•+} and the uptake of the proton by another molecule of AcrH₂. This was confirmed by experiments in the presence of pyridine (see below).

The two reduction peaks seen in Fig. 3 can be assigned to the proton (about 0 V) and AcrH⁺ (-0.5 V [9]), respectively, which is formed upon the two electron oxidation of AcrH₂.

We investigated the electrochemical oxidation of the compounds **1a**, **1c**, **2c**, **2d**, **3d** and **1e** in more details. The results presented are strongly different to those described for AcrH₂ and not in accordance with the ECE-mechanism.

According to the ECE-mechanism the formation of **4** at the anode should be detectable by the reduction peak of these cations. Indeed, the reduction peak between -0.2 V and -0.3 V observed with **1a** and **2c** (Fig. 2) is attributed to the corresponding tropylium ions since the reduction peak in the cyclic voltammogram of neat **4a** and **4c** is located at this potential. The cyclic voltam-

mogram of the isomer **2d** also possesses a reduction peak at -0.5 V which is assigned to **4d** (see Fig. 2(e)). Notably, the height of the cathodic peaks is much lower than the half of the oxidation peaks.

Surprisingly, the isomeric compound **3d** does not exhibit the reduction wave of **4d** (Fig. 4 a). The tropylium cation **4d**, provided it will be formed, can also be detected by its reversible oxidation peak of the dimethylamino group ($E_{\text{ox}} = 1.07$ V; see Fig. 4a). The cyclic voltammograms of compound **3d** were measured at various concentrations and scan rates, respectively. It turned out that at higher concentrations and at the lower scan rate the formation of **4d** becomes visible by the oxidation peak at 1.1 V as it is depicted in Fig. 4. This indicates that the formation of the two electron oxidation product depends on the concentration of **3d** and on the time between the initial and the second oxidation. This result corresponds to a rather slow formation of **4d**.

Furthermore, the cyclic voltammograms of **1a**, **2c**, **1d**, **2d** and **3d**, respectively, (see Fig. 2a, Fig. 2b, Fig. 2c, Fig. 2d and 4a) contain reduction peaks at a poten-

tial more positive than that of the tropylium ion. In the case of **1a** this reduction peak is assigned to a proton as is confirmed by measurements at the rotating glassy-carbon ring disc electrode. Besides protons further reduction peaks were detected in the case of **2c**, **2d** and **3d** indicating the formation of not yet identified products. Therefore the question arises how this unknown products are connected with the formation of **4**.

Cyclic Voltammetry in the Presence of a Base

AcrH₂

In the presence of pyridine the oxidation peak height is doubled (see Fig. 3). At the same time a shift of the potential occurs. A shift is expected if protons were released and subsequently scavenged by pyridine. The height of the reduction peak assigned to AcrH^+ is also doubled. According to the EC-DISP1-mechanism of this oxidation process [3, 10] pyridine displaces AcrH_2 in supporting the deprotonation of the radical cation and prevents the protonation of starting material.

Cycloheptatrienes

It was checked whether the anodic peak potential and the peak height of cycloheptatrienes compiled in chart 1 undergo changes when pyridine is present in the solution at a concentration of 10^{-2} M, *i.e.* at a concentration exceeding that of the cycloheptatriene compounds by a factor of 10. It turned out that apart from **2d** this is not the case.

2d

The behaviour of **2d** partly resembles an ECE-mechanism. Upon addition of pyridine the reduction peak of the radical cation is decreased (see Fig. 5). The oxidation peak increases at the same extent as the reduction peak becomes smaller. The reduction peak of **4** is in-

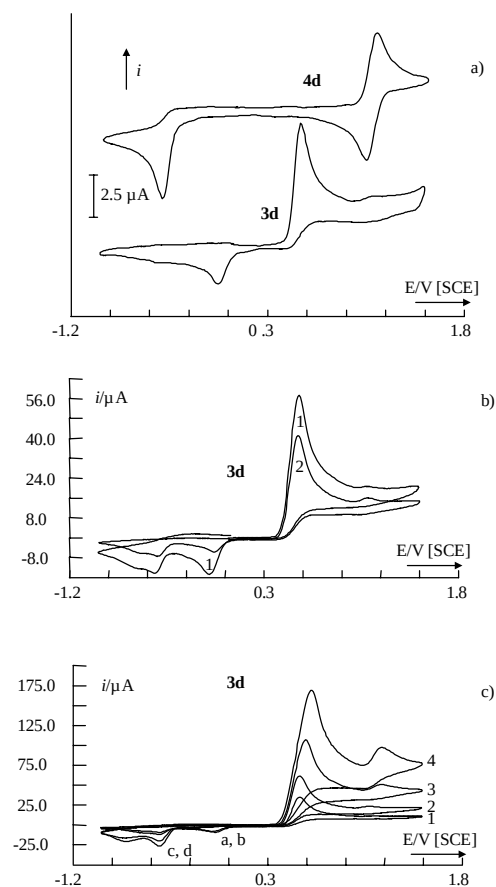


Fig. 4 Cyclic voltammograms of **3d** recorded in 0.1M $\text{Bu}_4\text{NPF}_6\text{-CH}_3\text{CN}$ solution. a) compounds **3d** and **4d**, concentration = 10^{-3} M, b) [**3d**] = 10^{-2} M; 1: 1 V s^{-1} , 2: 0.5 V s^{-1} , c) scan rate 0.5 V s^{-1} ; 1: [**2d**] = 5×10^{-3} M, 2: [**2d**] = 1×10^{-2} M, 3: [**2d**] = 5×10^{-2} M, 4: [**2d**] = 5×10^{-2} M.

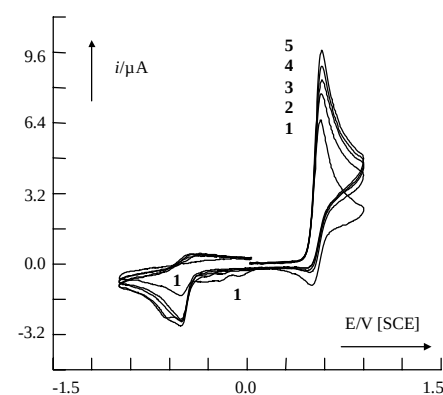


Fig. 5 Cyclic voltammograms (platinum electrode, $d = 1$ mm, scan rate 1 V s^{-1}) of **2d** (10^{-3} M) observed upon addition of pyridine. 1: without pyridine; 2: [pyridine] = 10^{-3} M; 3: [pyridine] = 2.5×10^{-3} M; 4: [pyridine] = 5×10^{-3} M; 5: [pyridine] = 10^{-2} M.

creased upon addition of the base. But, even at a ten-fold excess of pyridine the peak height attributed to the radical cation is only increased by 50%

Peak Heights

Provided the ECE-mechanism is valid a two-electron oxidation of all cycloheptatriene derivatives would be expected especially in the presence of a base such as pyridine. In the absence of pyridine in each case much less than $2F \text{ mol}^{-1}$ were transferred as shown by comparing the peak height with that of the ferrocene/ferrocenium couple (see Table 1). An exception is represented by **1a** which was oxidised by consuming $1.6 F \text{ mol}^{-1}$. The presence of pyridine has no influence on the peak height. As mentioned above only in the case of **2d** the peak height is slightly increased. On the other side, also at high scan rates irreversible cyclic voltammograms are obtained. Such behaviour is expected if a rapid follow-up reaction of the radical cation takes place. Deprotonation cannot be involved in this fast reaction because in this case a two electron oxidation should be observed.

Moreover, the peak current (and the transferred charge by comparing with the ferrocene/ferrocenium couple under the same conditions) measured for **1a**, **1c** and **1e** at the rotating platinum disk electrode depends on the rotation speed as it is shown in Table 2. These experiments indicate an approach to a two-electron oxidation process only at the low rotation speed. Accordingly, the peak current of the cyclic voltammogram of compound **1a** and **1c** depends on the scan rate in a manner that does not fulfil the Randles-Sevcik-equation [11] (see

Table 3). The peak current is less increased as calculated for higher scan rates. This can be explained by assuming a follow-up reaction of an intermediate product formed by the radical cation reaction. Obviously, the rate constant of this reaction yielding oxidizable products is in the range of the scan rate of cyclic voltammetry.

The experiments described above clearly show that the chemically irreversible oxidative electrochemistry is caused by reactions of the radical cations which do mainly not lead to the cycloheptatrienyl radicals, at least in the case of the aryl cycloheptatrienes. From the concentration dependent cyclic voltammograms obtained with **3d** (Fig. 4) a bimolecular follow-up reaction can be concluded.

Rotating-Ring-Disk Electrode (RRDE) Experiments

To get further insight into these bimolecular follow-up reactions of the radical cations and the nature of the unknown products detected by means of cyclic voltammetry we employed the RRDE to study the behaviour of **1a**, **1c**, **2c**, **2d** and **3d**, respectively. Glassy-carbon-electrodes were used in order to shift the reduction potential of protons to values more negative than of those the tropylium ions thus separating reduction peaks of intermediates, products **4** and protons, respectively. It turned out that only in the case of **2c**, **2d** and **3d** besides the tropylium ions and protons additional reducible products were detected at around 0 V (Fig. 6).

RRDE-experiments at different concentrations and rotation speeds, respectively, could only be carried out using **2d** and **3d** because electrode-coverage occurs in the case of the compounds **c**.

3-(*p*-Dimethylaminophenyl)-cyclohepta-1,3,5-triene **3d**

In Fig. 7 the ring current voltammograms ($i_{\text{ring}} = f(E_{\text{ring}})$) recorded at $[3d] = 10^{-4} \text{ M}$, 10^{-3} M and $5 \times 10^{-3} \text{ M}$ and at three rotation speeds of the RRDE are depicted. The ring potential is scanned from -1.0 V to 0.5 V (SCE). Without any potential at the disk electrode the voltammogram of compound **3d** in this range is recorded at

Table 2 Number of transferred charges measured in acetonitrile solution (10^{-4} M) at the rotating platinum disk electrode (calibrated with the ferrocene/ferrocenium couple) (ω = rotation speed)

ω/s^{-1}	$F \text{ mol}^{-1}$		
	1a	1c	1e
63	2.0	1.6	1.5
314	1.6	1.2	1.1

Table 3 Limiting peak current (i_p^a) of **1a** and **1c** in dependence on the scan rate v in comparison to ferrocene ($c = 10^{-3} \text{ M}$)

v/Vs^{-1}	ferrocene		1a			1c	
	$i_p^a/\mu\text{A}$	$I_p/v^{1/2}c \times 10^{-3} [7]$	$i_p^a/\mu\text{A}$	$I_p/v^{1/2}c \times 10^{-3} [7]$	$F/\text{mol}^a)$	$i_p^a/\mu\text{A}$	$F/\text{mol}^a)$
1	6.70	6.7	10.78	10.8	1.61	6.26	0.93
2	9.49	6.7	15.00	10.6	1.58	8.48	0.89
5	14.67	6.6	22.01	9.9	1.50	12.57	0.86
10	20.79	6.5	30.93	9.8	1.49	16.95	0.82
20	28.89	6.5	41.25	9.2	1.43	23.69	0.82
50	45.34	6.5	58.82	8.3	1.30	37.22	0.82

^{a)} according to $1F/\text{mol}$ of the ferrocene/ferrocenium couple

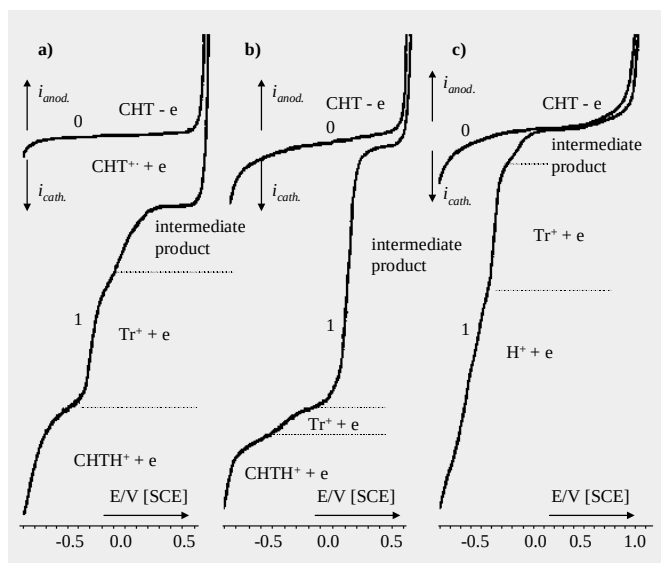


Fig. 6 RRDE-voltammograms of **2c**, **2d** and **3d** (10^{-4} M) in 0,1M $\text{Bu}_4\text{NPF}_6\text{-CH}_3\text{CN}$ solution, rotation speed $\omega = 104.7 \text{ s}^{-1}$.

the ring electrode (Fig. 7, curves 0). If the disk potential is maintained at a constant potential of 0.8 V the oxidation of **3d** will take place at this electrode. Oxidation products are transferred to the ring electrode due to the rotation of the RRDE and are reduced there.

At $[\mathbf{3d}] = 10^{-4} \text{ M}$ (Fig. 7a) even the radical cation of **3d** is visible. **4d** detected by the small wave at -0.4 V

may be formed via the ECE-mechanism. Notably, no **4d** but a reduction wave of the intermediate product at 0.2 V is monitored in the concentration range between $5 \times 10^{-4} \text{ M}$ and $2.5 \times 10^{-3} \text{ M}$ (Fig. 7b). Only at concentrations $> 2.5 \times 10^{-3} \text{ M}$ the reduction wave assigned to **4d** is indicated (Fig. 7c).

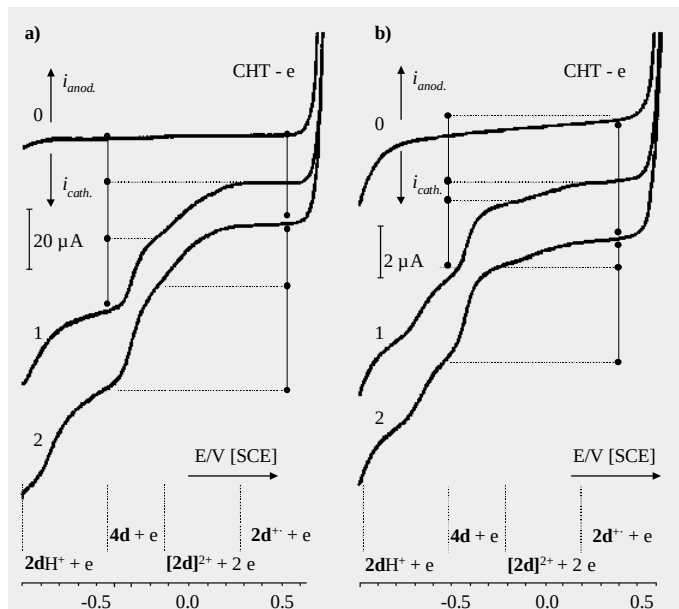


Fig. 8 **2d**-RRDE voltammograms in 0,1M $\text{Bu}_4\text{NPF}_6\text{-CH}_3\text{CN}$ solution (glassy-carbon electrodes)
a) $[\mathbf{2d}] = 10^{-3} \text{ M}$; b) $[\mathbf{2d}] = 10^{-4} \text{ M}$. 0: $E_d = 0 \text{ V}$, 1: $E_d = 0.8 \text{ V}$, $\omega = 104.7 \text{ s}^{-1}$, 2: $E_d = 0.8 \text{ V}$, $\omega = 209.4 \text{ s}^{-1}$.

1-(*p*-Dimethylaminophenyl)-cyclohepta-1,3,5-triene **2d**

In the RRDE-voltammogram of **2d** (see Fig. 8) three reduction waves can be assigned to the radical cation, the intermediate product, **4d** and the protonated **2d**, respectively (it was proven that protonated **2d** exhibits a reduction wave at this potential). In the case of the 1-isomer of compound **d** the formation of **4d** via deprotonation of the longer living radical cation of **2d** (ECE-mechanism) is able to compete with the formation of the intermediate product.

It is seen from Fig. 8 and Table 4 that the limiting current attributed to the radical cation of **2d** decreases at increasing concentration of **2d** due to deprotonation of the radical cation by **2d** which acts as the base. The concentration of the intermediate product raises at the higher concentration of **2d** confirming the bimolecular formation of this intermediate. Despite of variable concentration ratios of the radical cation and the intermediate product the portion of **4d** is nearly constant.

For compound **2d** the collection efficiency [12] $N_k = [i_r/i_d]$ (i_r and i_d : currents measured at the ring and the disk, respectively) was measured. It turned out (see

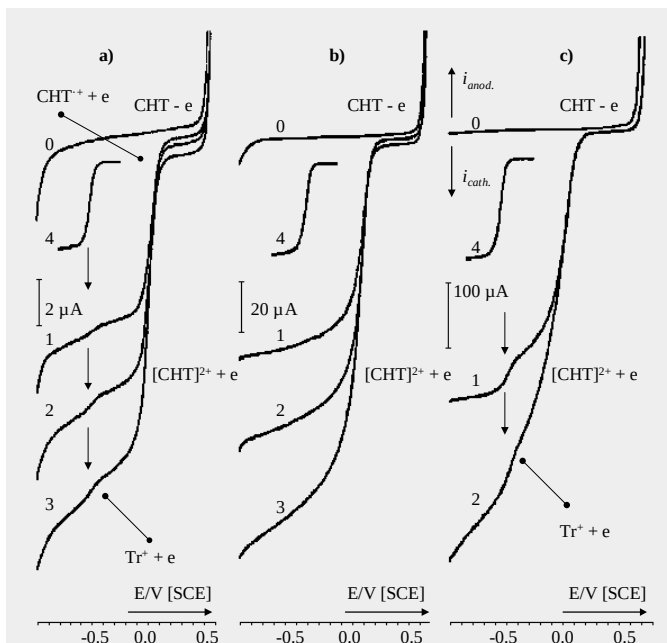


Fig. 7 **3d**-RRDE-voltammograms in 0,1M $\text{Bu}_4\text{NPF}_6\text{-CH}_3\text{CN}$ solution (glassy-carbon-electrodes)
a) $[\mathbf{3d}] = 1 \times 10^{-4} \text{ M}$; b) $[\mathbf{3d}] = 10^{-3} \text{ M}$; c) $[\mathbf{3d}] = 10^{-2} \text{ M}$. 0: $E_d = 0 \text{ V}$, 1: $E_d = 0.8 \text{ V}$, $\omega = 104.7 \text{ s}^{-1}$; 2: $E_d = 0.8 \text{ V}$, $\omega = 209.4 \text{ s}^{-1}$; 3: $E_d = 0.8 \text{ V}$, $\omega = 418.9 \text{ s}^{-1}$; 4: voltammogram at the ring electrode upon addition of **4d**

Table 4 Limiting currents of the waves of **4d** and the intermediate product (IP) observed for **2d** at the RRDE (glassy-carbon).

[2d]/ 10 ⁻³ M	ω/s^{-1}	$i_{disc}/\mu A$	$I_{4d}/\mu A$	$\frac{i_{4d}^{a)}}{i_{disc}}$	$i_{IP}/\mu A$	$\frac{i_{IP}^{a)}}{i_{disc}}$	$i_{2d^{+}}/\mu A$	$\frac{i_{2d^{+}}^{a)}}{i_{disc}}$
1,00	104.7	230	21.5	0.093	17.0	0,076	16.50	0,072
	209.4	316	28.0	0.089	21.0	0,066	30.50	0,097
0,75	104.7	173	15.8	0.091	11.75	0,068	13.75	0,079
	209.4	240	22.0	0.092	14.0	0,058	25.75	0,107
0,5	104.7	122	12.0	0.098	7.0	0,060	9.00	0,082
	209.4	172	15.5	0.090	8.0	0,049	17.75	0,112
0,25	104.7	57	5.5	0.096	2.9	0,051	5.70	0,100
	209.4	77	7.0	0.091	3.2	0,042	10.40	0,135
0,1	104.7	22	2.9	0.129	0.5	0,023	2.40	0,109
	209.4	30	3.1	0.102	0.7	0,018	4.60	0,153
0,075	104.7	16	1.8	0.112	0.3	0,019	2.00	0,125
	209.4	22	1.9	0.086	0.25	0,015	3.80	0,173

^{a)} normalized currents which are proportional to the concentration of the species

Table 5 Collection efficiency N_k ^{a)} measured with **2d** at the RRDE [ring potential $E_R = 0.2$ V (SCE); disc potential $E_d = f(t) = 0.2... 0.8$ V]

Rotation rate ω/s^{-1}	1.0×10^{-4} M	5.0×10^{-4} M	1.0×10^{-3} M
104.7	0.0527	0.0699	0.1081
209.4	0.0714	0.0880	0.1261
314.2	0.0800	0.1014	0.1411
418.9	0.0892	0.1117	0.1525
523.6	0.0950	0.1233	0.1624

^{a)} calibrated with the ferrocene/ferrocenium couple ($N_0 = 0.2600$; theory: $N = 0.2629$ [12])

Table 5) that N_k depends both on the concentration of **2d** and the rotation rate of the electrode. This behaviour is usually observed if a chemical bimolecular follow-up reaction is consuming the product of the electrochemical reaction at the disc electrode forming a species which is not electroactive at the ring [12]. Thus, it is confirmed, that the lifetime of the radical cation formed from **2d** at the electrode surface is concentration dependent. This dependence of the concentration of the radical cation (measured as limiting current) on

the concentration of **2d** is non-linear as expected for a dimerisation mechanism (see Fig. 9) [13].

RRDE in the Presence of a Base

3-(*p*-Dimethylaminophenyl)-cyclohepta-1,3,5-triene **3d**

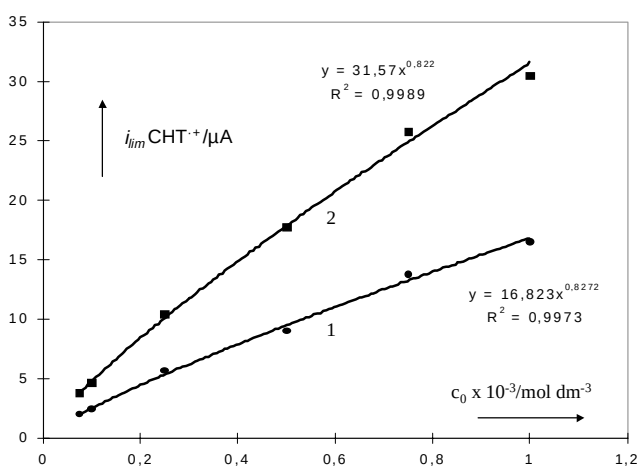
In the presence of pyridine **4d** was formed also at 10^{-3} M of **3d** (see Fig. 10a). The higher the pyridine concentration the higher is the wave attributed to **4d**. At the same time a reaction between pyridine and the intermediate product takes place (which is reduced at $E_p^c = -1.3$ V according to CV) thus diminishing the wave of the intermediate product without an equivalent increase of the wave of **4d**. By replacing pyridine by 2,6-di-*t*-butyl-4-methyl-pyridine this reaction is prevented.

1-(*p*-Dimethylaminophenyl)-cyclohepta-1,3,5-triene **2d**

Upon addition of pyridine the wave assigned to the intermediate product is decreased (see Fig. 10b). At the same time the reduction wave attributed to **4d** is increased indicating the formation of **4d** via the intermediate product supported by the base.

Controlled Potential Electrolysis

The electrochemical oxidation of **1c**, **1d**, **2d**, **3d** and **1e**, respectively, was attempted at a (constant) anode potential being slightly more positive than the oxidation peak potential. In the case of **1c** and **1e** a total charge

**Fig. 9** Dependence of the limiting current of the radical cation of **2d** on the concentration of **2d** at different rotation speeds of the RRDE: 1: $\omega = 104.7$ s⁻¹, 2: $\omega = 209.4$ s⁻¹

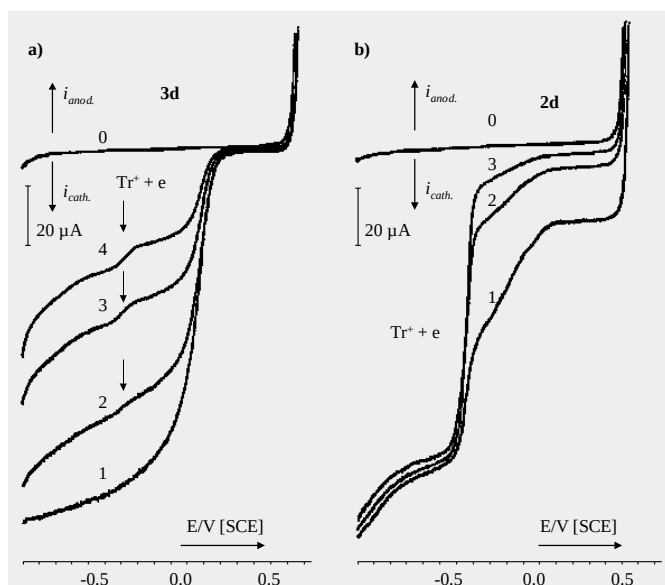


Fig. 10 RRDE voltammograms of **2d** and **3d** in 0,1M Bu₄NPF₆-CH₃CN solution (glassy-carbon electrodes) upon addition of pyridine, $\omega = 104.7 \text{ s}^{-1}$ ^a) [**2d**] = 10⁻³ M; 1: [**2d**] = 10⁻³ M, [pyridine] = 10⁻³ M, 2: [**2d**] = 10⁻³ M, 3: [pyridine] = 5 × 10⁻³ M; b) 1: [**3d**] = 10⁻³ M; 2: [**3d**] = 10⁻³ M, [pyridine] = 10⁻³ M, 3: [**3d**] = 10⁻³ M, [pyridine] = 5 × 10⁻³ M, 4: [**3d**] = 10⁻³ M, [pyridine] = 10⁻² M.

Table 6 Yields of tropylium salts by electrolysis of the corresponding cycloheptatrienes using a constant anode potential (E_A)

Compound	E_A /V	Yield/%
1c	1.2	84
1d	0.7	15
2d	0.7	84 ^a)
3d	0.7	80 ^a) (96 ^b))
1e	1.5	73

^a) addition of pyridine, ^b) addition of 2,6-di-*t*-butyl-4-methylpyridine

consumption of 2F mol⁻¹ resulted in the conversion of the cycloheptatrienes into the corresponding tropylium ion with high yields (see Table 6).

Also **2d** and **3d** were converted into the corresponding tropylium ion, but in these cases the reaction came to an end at a conversion of about 50%.

Pyridine at a concentration of 10⁻³ M exerted a pronounced influence on the yield of **4d** during the electrolysis of **2d** and **3d**. Total conversion of **2d** or **3d** into **4d** was achieved with a charge consumption of 2F mol⁻¹ in the presence of pyridine, which gives rise to the assumption that pyridine scavenges protons that otherwise add to **2d** or **3d** and prevent their oxidation.

Noticeably, **1d** behaved differently: the reaction leveled off at about 50% conversion in the absence of pyridine but the corresponding tropylium ion was not formed. This finding conforms to the cyclic voltammogram (Fig. 2c) which contains a reduction peak at

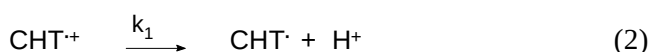
-0.4 V but no peak at the potential of **4d** (-0.52 V). The reaction product which could not be isolated and identified, absorbs light around 420 nm. Interestingly, **4d** was formed to some extent (about 15%) upon heating the electrolysis solution of **1d** to 60 °C (after the electrolysis at room temperature).

Discussion

According to the results of the electrolysis compound **1d** is the exception of the rule because only a very small yield of **4d** was obtained in contrast to its isomers **2d** and **3d**. This finding emphasizes that the radical cation within the seven membered ring is the prerequisite of the tropylium ion formation by electrochemical oxidation. Both the conjugated isomers **2d** and **3d** and the other compounds **1** fulfil this criterion.

Obviously, the deprotonation reaction of the radical cations of arylcycloheptatrienes (reaction (2)) plays only a minor role. According to the RRDE-experiments the first electron transfer occurring at the anode is followed by a homogeneous, bimolecular reaction leading to an intermediate product which is reduced at a more positive potential than the corresponding tropylium cation. A dimerisation reaction can be assumed according to the results obtained with compounds **2d** and **3d**. The other arylcycloheptatrienes considered here may behave in the same way according to the finding that in all cases only 1F is transferred at the electrode. The linear dependency of the peak potentials of these compounds on the substituent constant σ_p supports the assumption of only one mechanism valid also in the case of the other arylcycloheptatrienes. In the case of the parent compound **1a** the mechanism of the oxidation process might differ from that of the other compounds.

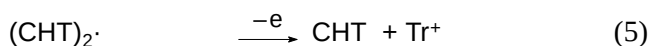
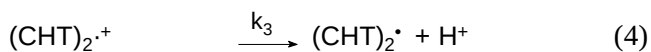
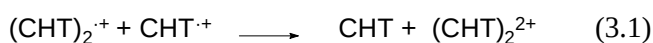
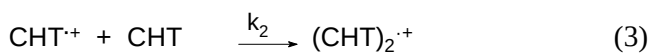
The exponent of the non-linear dependence of the limiting peak current (related to the concentration of the radical cation) of compound **2d** on the concentration of **2d** (Fig. 9) was determined to be 0.8. Assuming a DIM1 and a DIM2 (DISP) mechanism, respectively, of the bimolecular reaction of the radical cation this exponent is expected to be 0.66 [13]. The difference obtained may be attributed to the competition of the ECE-mechanism and the disproportionation discussed below. Reaction (7) yields back the starting material.



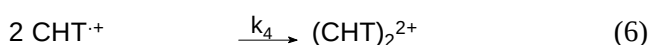
Regarding the mechanism of the formation of **4** via a bimolecular reaction of the radical cation two different

mechanisms may generally be discussed [10]:

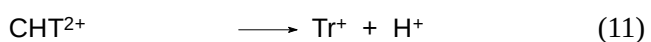
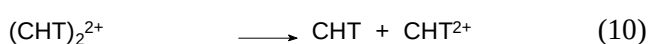
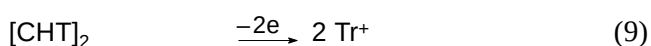
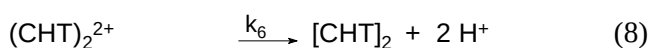
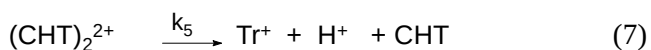
(A) Radical-substrate-coupling (RSC or DIM2)



(B) Radical-radical-coupling (RRC or DIM1)



A priori, the formation of the tropylium ion is possible on different ways (reactions (7) – (11)).



(CHT = cycloheptatriene derivative; Tr^+ = tropylium cation)

A clear differentiation between the two dimerization mechanisms is generally difficult [14] and not possible in our case because the kinetic analysis is disturbed by complicated succeeding and competing reactions.

A reversibility of the reaction (6) monitored with other radical cations [15] was not observed in the case of **2d** which is approaching a quasi-reversible behaviour at the higher scan rates (see Fig. 2e). The formation of the tropylium ions *via* the monomeric dication [reactions (10) and (11)] is rather unlikely because the intermediate species are detected even in the presence of pyridine.

The dimeric, distonic radical cation formed in reaction (3) might be a candidate for a reducible intermediate. But, according to mechanism (A) only 0.5 F mol⁻¹ would be consumed to form this radical cation. As it has been shown above the peak current of the first oxidation step corresponds to at least 1 F mol⁻¹. According to the collection efficiency found in the RRDE-experiment carried out with **3d** the intermediate product is formed with quantitative yield consuming 1F/mol at the disc-electrode. Furthermore, according to (5) the second electron must be abstracted at the anode. Such a

second oxidation peak which can be expected at a slightly higher potential than the first one [16] was not observed.

Mainly process (6), *i.e.* the formation of the dication, are likely to be responsible for the irreversibility of the electrode reaction. The formation of this dication *via* reaction (3.1) can not completely be excluded. But at high electrolyte concentrations reaction (6) is more plausible than reaction (3) [17]. Therefore, the RSC-mechanism seems to be rather implausible.

The dication can be reduced yielding the observed reduction wave more positive than the reduction wave of **4**.

The second electron transfer leading to the tropylium ion does not occur at the electrode surface but by process (7), *i.e.* by disproportionation yielding back the starting material besides the cation and the proton. This reaction is initiated by a slow deprotonation (compared with the scan rate used in cyclic voltammetry) of the dication. Therefore, pyridine has an influence only on the formation of the cation formed from the intermediate dication. According to the authors knowledge so far such disproportionation reaction of a dication was not described. In other systems the deprotonation of the dication [17] or the reaction with nucleophiles lead to stable products [14].

Reactions (8) and (9) as an alternative formation sequence are unlikely because the formation of the known dimers $[\text{CHT}]_2$ [6] was not observed during the electrolysis described below.

The intermediate dication could not be detected when studying compound **1a**. The absence of the dication is in accordance with the finding that in this case the highest charge transfer rate was observed at the anode.

Different results obtained with the investigated cycloheptatrienes may be attributed to different rate constants of the reaction sequence, which depend on the nature of the compound:

In the case of **1a** k_5 seems to be relatively high. Thus, cycloheptatriene is formed at the anode causing an increased height of the oxidation peak. The intermediate dimeric dication is very unstable thus not allowing to be detected within the time scale investigated here.

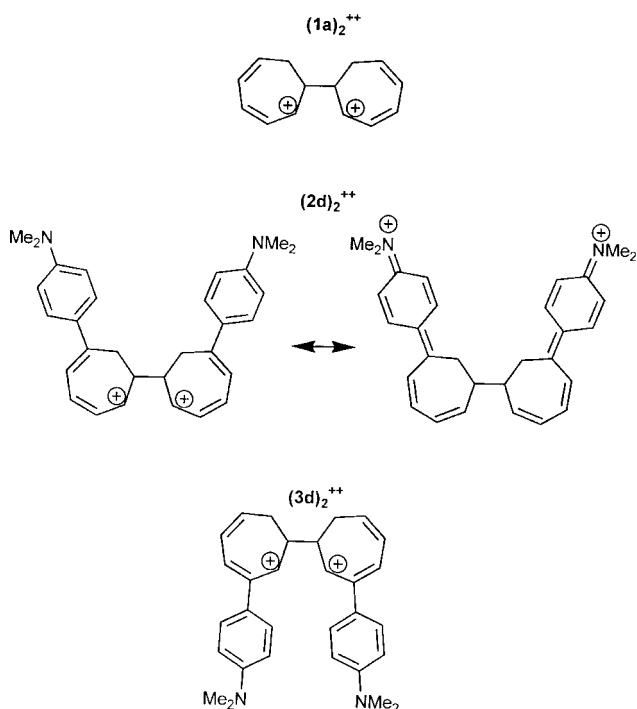
Aryl substituents at the seven-membered ring stabilize these intermediates which are detected in the case of **2c**, **2d** and **3d**.

Compound **2d** is the only cycloheptatriene derivative which approaches a quasi-reversible cyclic voltammogram at high scan rates. In this case k_4 is small and in the range of the deprotonation rate constant k_1 . Therefore, competition between dimerization and deprotonation is observed. Pyridine deprotonates both the radical cation of **2d** and the intermediate dimeric dication. Both reactions increase the concentration of oxidizable material at the anode (**2d** and **2d'**) thus increasing the peak

height in the cyclic voltammogram of **2d**.

In the case of the other cycloheptatriene compounds the dimerization seems to be much faster than the deprotonation of the primarily formed radical cation.

The different rate constants may be attributed to the different structure of $(\text{CHT})_2^{2+}$ (see Scheme 1 for hypothetical dimers). Quantum mechanical calculations (PM3) have shown that such dimers indeed have energy minima.



Scheme 1

The disproportionation reaction is supported by deprotonation of the dication. Therefore, the addition of pyridine leads to an increase of the concentration of the tropylium ion as it was demonstrated with compounds **2d** and **3d** (see Fig. 10). In the absence of pyridine compound **3d** plays the role of the base (see Fig. 4 and compare Fig. 7b and 7c).

Pyridine scavenges protons released according to reaction (7) and thus prevents the protonation of **2d** and **3d**.

The protonated species **2dH⁺**, **3dH⁺** are not convertible into **4d** at the potential appropriate for the oxidation of **2d** and **3d**. The protonated **2d** has an oxidation peak potential of 1.6 V and can be reduced releasing the proton at -0.6 V (platinum electrode).

The different findings of the cyclic voltammetry and the coulometry regarding the transferred charges must be explained by the different time scales of the two methods.

Conclusion

1. This paper demonstrates that the electrochemical oxidation of aryl-substituted cycloheptatrienes proceeds preferably by a RRC-mechanism. The process is governed by the chemical nature and the position of the aryl substituent.
2. At the electrode only one electron is transferred. Dimerization of the radical cations and disproportionation of the dimeric dication yielding the tropylium salt and the starting material are postulated.
3. Electrolysis of aryl substituted cycloheptatrienes affords the corresponding tropylium cations with high yields. In the case of *p*-dimethylaminophenyl-cycloheptatriene only the 1- and 3-isomers are effectively oxidised. The *p*-dimethylaminophenyl substituent in the 7-position of the seven-membered ring hinders the electrochemical oxidation to the tropylium salt.

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Experimental

Rapid scan (1 to 50 V s⁻¹) cyclic voltammetry was performed using a PG 285 IEC (HEKA Elektronik) potentiostat and an EG&G cell having a planar platinum working electrode (*d* = 1 mm) combined with the program "Electrochemistry. IBM V 3.1". A saturated calomel reference electrode (in a luggin capillary with diaphragm) was employed. Acetonitrile (HPLC grade) was obtained from Riedel de H  en and purified and carefully dried according to standard procedures. Tetrabutylammonium hexafluorophosphate (10⁻¹ M, Fluka, dried at 110   C) was used as supporting electrolyte. Oxygen was removed by argon purging.

For the ring-disk experiments a teflon-platinum ring-disk electrode [*r*₁ = 2.300 cm; *r*₂ = 2.425 cm; *r*₃ = 2.725 cm, *N*₀ = 0.2600 (calibrated with ferrocene and diphenylpicrylhydrazyl)] or a teflon-glassy-carbon-ring-disc-electrode (*r*₁ = 2.850 cm; *r*₂ = 3.125 cm; *r*₃ = 3.975 cm, *N*₀ = 0.3980) was used. The electrodes were operated by an electrode rotator Model 636 (Princeton Applied Research) combined with a double-potentiostat PG 287 (Heka Elektronik). In order to obtain *N_K* values, the disk current was varied stepwise between zero and the limiting current of the first anodic wave. The ring electrode was maintained at a controlled potential of 0.35 V (SCE) so that no ring current was obtained with the disk current being zero.

Electrochemistry was carried out by using the PG 285 potentiostat connected to a nitrogen-purged three-electrode-cell fitted vs. a SCE with a platinum gauze working electrode and a platinum auxiliary electrode, the latter separated from the working electrode by a porous-glass disk. 100 mmol of **1** were added to 50 ml solution of 0.1M tetraethyl ammonium perchlorate. Electrolysis was performed at a constant potential and was terminated when the initial current (15–20 mA) was lowered to 0.75 mA. Yields of the tropylium salts were deter-

mined by HPLC by calibrating of the peak areas with the help of samples of known concentration. Absorption spectra were recorded on a Shimadzu UV-2101 PC spectrophotometer. **1a** (Merck) was purified by repeated rectification. The cycloheptatrienes **1b** – **1g** [18] and **3d** [19], **2d** [20], **3c** [21], **2e** [22] and **3e** [22] and the tropylium perchlorates **4** [18] were synthesised as described in the literature and were purified by recrystallization. **1h** [23] and **1i** [20] were available according to standard procedures.

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