THE POLAROGRAPHIC REDUCTION OF SOME ARENOTROPILIDENES ARENOTROPONES AND THEIR CHROMIUM AND IRON TRICARBONYL COMPLEXES IN DMF

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SUMMARY: The electro reduction of some arenotropilidenes and their chromium and iron tricarbonyl complexes in DMF were found to proceed by two electrons represents by one wave, producing the corresponding dianion. The polarograms of arenotropones and their chromium tricarbonyl complexes in DMF consist of two successive reduction waves, each corresponds to 1 F/mol. The reduction mechanism was investigated as well as the number of electrons was determined. Also, the half wave potentials of the ligands were compared with those of their metal tricarbonyl complexes.

Key Word: Polarography.

INTRODUCTION

In the course of our research on the electrochemical reduction of arenotropones (1, 2) and arenotropolones (3), this investigation is devoted to report the electrochemical behavior of a variety of arenotropilidenes, arenotropones and their chromium and iron tricarbonyl complexes in DMF.

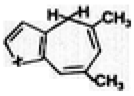
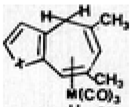
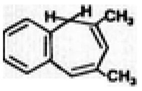
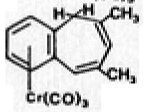
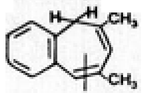
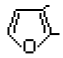
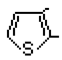
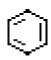
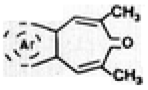
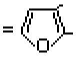
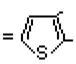
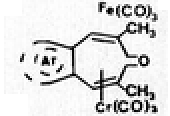
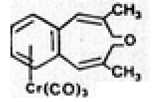
Although a few number of papers have appeared in the literature regarding the non-aqueous electrochemical reduction of arene tricarbonyl chromium complexes (4–8), no detailed study has appeared considering the reductive electrochemical characteristics of arenotropilidenes and their metal tricarbonyl complexes.

Gubin has reported that the polarographic reduction of acetophenone chromium tricarbonyl occurs by electrode reversible one electron process (6,7). In contrast, Dessy *et al.* (4) reported transferring two electrons per molecule of benzene chromium tricarbonyl during an exhaustive controlled potential reduction.

EXPERIMENTAL

The synthesis of arenotropilidenes, arenotropones and their metal complexes, Table 1, were attempted by El Borai (9,10). Their purity and structure were checked by m.p. determination, ^{1}Hnmr, elemental analysis and thin-

Table 1

I X = O II X = S		I$_a$ M = Cr I$_b$ M = Fe II$_a$ M = Cr II$_b$ M = Fe	
III		III$_a$	
		III$_b$	
IV Ar =  V Ar =  VI Ar = 		IV$_a$ Ar =  V Ar =  VI	
			

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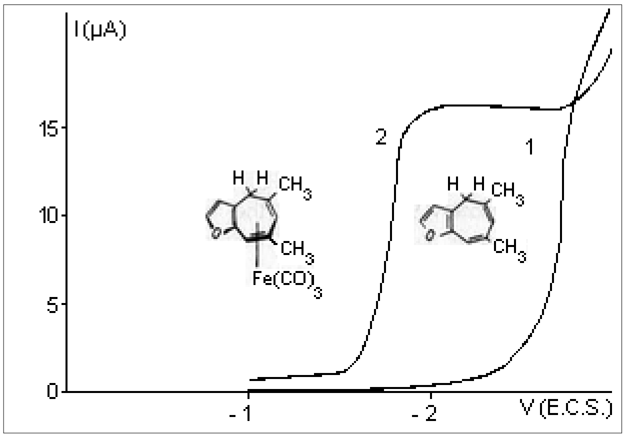
layer chromatography. The polarograms were recorded using a Tacussel 'Tipol' with three electrodes. A saturated calomel electrode was used as: reference electrode. A solution containing 0.1 ML^{-1} of N-tetrabutyl ammonium per chlorate was used as supporting electrolyte. A series of Thiel buffer solutions were used at a μ 0.1 M.

RESULTS AND DISCUSSION

The polarograms of arenotropilidenes (I–III) in DMF consist of one reduction wave (A), Figure 1, corresponding to 2 F/mol which shifts to less negative potentials when complexes with chromium or iron tricarbonyl (I_2–III_a), Table 2. On the other hand, the polarograms of arenotropones (IV–VI) and their chromium tricarbonyl complexes (IV_a–VI_a) in DMF consist of two successive reduction waves (B,C) of equal heights, each corresponds to 1 F/mol.

The values of n were determined coulometrically under controlled potential (31). The wave (A) exhibits two electrons while each of the waves (B) and (C) corresponds to one electron, Table 2.

Figure 1: Polaragramme of 5,7-dimethyl 4H-cyclohepto [6] furan (1) and 4,7-dimethyl 4H-cyclophepto (6) furan iron tricarbonyl (2) in dimethylformamide.



Analysis of the wave was carried out by applying the fundamental equation for polarographic data (12). The correlations of E with $\log[{}^{i}/\,i_1-i]$ are straight lines with somewhat varying slopes. Using the values of slope,

Table 2: Polarographic results obtained for compounds I-VI.

Compound	$-E_{1/2}$(V)	(a) $E_{1/2}$ (V)	1(μ A)	log i/i-i slope of E	∝ n_a	n_a	∝
I	2.67		6.80	18.25	1.07	2.0	0.53
I_a	2.49	0.18	6.70	17.10	1.01	2.0	0.51
I_b	0.80	0.87	6.55	15.93	0.94	2.0	0.47
II	2.56		6.10	20.31	1.19	2.0	0.60
II_a	2.53	0.03	6.00	19.72	1.16	2.0	0.58
II_b	1.78	0.78	5.80	16.10	0.95	2.0	0.48
III	2.54		5.80	18.92	1.12	2.0	0.56
III_a	1.94	0.60	5.61	17.01	1.00	2.0	0.50
III_b	1.87	0.67	5.50	16.30	0.96	2.0	0.48
IV	1.86		1.85	16.60	0.98	1.0	0.98
	2.56		2.62	10.20	0.60	1.0	0.60
IV_a	1.85	0.01	2.63	16.52	0.97	1.0	0.97
	2.55	0.01	2.40	9.82	0.58	1.0	0.58
V	1.88		3.25	16.08	0.95	1.0	0.95
	2.42		3.10	10.21	0.63	1.0	0.63
V_a	1.78	0.10	3.13	15.58	0.92	1.0	0.92
	2.23	0.19	2.96	9.80	0.58	1.0	0.58
VI	1.74		2.53	16.31	0.96	1.0	0.98
	2.40		2.48	11.20	0.66	1.0	0.66
VI_a	1.56	0.18	2.41	15.87	0.94	1.0	0.94
	2.53	-0.13	2.39	10.81	0.64	1.0	0.64

Table 2, the values of the transfer coefficient α and can be calculated. Waves (A) and (C) proceed irreversibly or quasi reversibly according to the value of α. Wave (B) proceeds reversibly since the α values attain the unity.

Arenotropones may have two centers for reduction, the carbonyl group and the tropilidene ring, which also may be an active center for reduction in arenotropilidenes.

Firstly, we wish to investigate the reduction of the tropilidene ring, and for this purpose a per chlorate salt of the type VII can be examined, but the unstability of this salt even in strong acidic media renders it difficult to carry out complete study on it. However, the salt VII $(C_{11}H_{11}S)^+$ ClO_4, was dissolved in Thiel buffer solutions of varying pH values.

In solutions of pH < 4, the polarograms consist of one reduction wave corresponding to 1 F/mol. Within the pH range 4–7, a second wave appears which almost has equal height as that of the first wave. At pH > 7, the polarographic characteristics are represented in Figure 2. These results are in accordance with those obtained by Khopin and Zhdanov (13), who studied the electro-reduction of tropylium per chlorate salt. The first wave can be attributed to the formation of a free radical which undergoes dimersation. At pH > 4, the new wave corresponds to the formation of thiophenotropilidene, since the reduction process involves the uptake of two electrons and one proton.

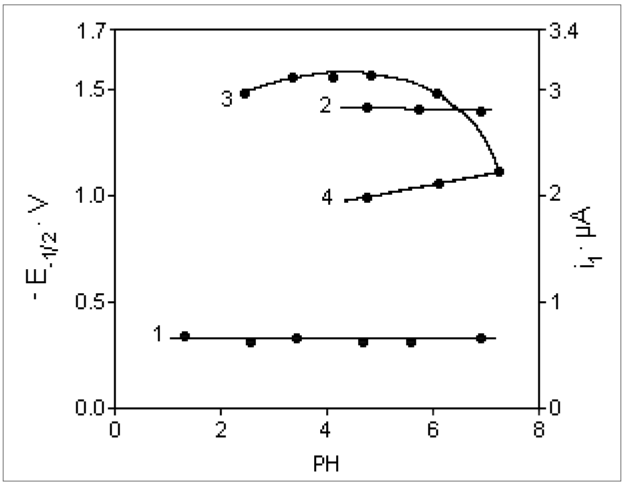
$(C_{11}H_{11}S)^+ + e \quad (C_{11}H_{11}S)$ first wave

$2(C_{11}H_{11}S) \quad (C_{11}H_{11}S)_2$ pH < 4

$(C_{11}H_{11}S)^+ + 2e \quad (C_{11}H_{11}S)$

$(C_{11}H_{11}S)^- + H^+ \quad C_{11}H_{12}S$ pH > 4

Figure 2: Plot of $E_{1/2}$ and is vs Ph for compound VII (0.5 nM).



At pH > 4, the final product of reduction is the thiophenotropilidene itself as was supported by electrolysis at controlled potential (14). The electrolysis was carried out in aqueous solution at pH = 6 and at −1.38 V. After the extraction of the product of electrolysis, it was analyzed by vapor phase chromatography, the electrochemical reduction was quantitative and the three isomers of compound VII were separated in the proportions of 5:75:20%.

These proportions are in agreement with those obtained chemically by Guilard and Fournari (15). Thus, the tropilidene rings inactive towards reduction in DMF under these experimental conditions.

The reduction of arenotropilidenes and their complexes in DMF produces the corresponding dianiouns (8).

In the case of arenotropones and their chromium tricarbonyl complexes, wave (B) corresponds to the direct reduction of the basic form to the anion radical i which reacts with one mole of the solvent to produce ii. Radical ii undergoes further reduction to form the alcohol iii.

$C = 0 + e \quad C - 0$ (i)

$(C - 0) + \text{solvent} \quad C - OH + \text{solvent}$ (ii)

$C - OH + e + \text{solvent} > CH - OH + \text{solvent}$ (iii)

The half wave potentials of the complexes I_a–VI_a, shift to less negative potential relative to the free ligand given a small displacement. The displacement in $E_{1/2}$ values for arenotropilidenes and their metal tricarbonyl complexes depends on both the nature of arenotropilidenes and the metal tricarbonyl. In the case of compound III_a the chromium tricarbonyl links the benzene nucleus, while in the case of compounds I_a and II_a, it links the tropilidene ring. These results were previously supported by ^{1}Hnmr and X-ray analysis (9,10).

The $E_{1/2}$ value for III-III_a is higher than that observed in the case of iron tricarbonyl complexes (8). The displacement observed for the iron tricarbonyl complexes I_b–III_b, is of the order with the values observed in the case of cyclooctatrien iron tricarbonyl complex (16).

The high values of $E_{1/2}$ of iron tricarbonyl complexes to that chromium complexes can be referred to the intense electron attracting effect of iron tricarbonyl group. On the other hand, the displacement in $E_{1/2}$ values for arenotropones and their chromium tricarbonyl complexes depends on the nature of arenotropones. In the case IV_a and V_a the chromium tricarbonyl group links the tropone ring while it links the benzene ring in the case of compound VI_a. This is due to the high electron density of benzene ring than the tropone nucleus.

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