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Anodic Oxidation Potentials of Aromatic Cyanoesters

Short Communication

Mohammad M. Al-Arab*, **Khaled R. Barqawi**, and **Hani D. Tabba'**
Chemistry Department, Yarmouk University, Irbid, Jordan

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Using cyclic voltammetry, the anodic oxidation potentials for a series of 15 substituted aromatic cyanoesters have been measured and analyzed. Irreversible anodic oxidations were observed, in addition to a cathodic reduction wave. The different aromatic species exhibited different potential values, in accordance with the type of the substituent and nature of the aromatic nucleus.

(Keywords: Cyanoester; Cyclic voltammetry; Oxidation potentials)

Anodische Oxidationspotentiale aromatischer Cyanoester (Kurze Mitteilung)

Unter Verwendung von cyclischer Voltametrie wurden die anodischen Oxidationspotentiale einer Serie von 15 substituierten aromatischen Cyanoestern gemessen und analysiert. Zusätzlich zu einer kathodischen Reduktionswelle wurden irreversible anodische Oxidationen beobachtet. Dabei zeigten die verschiedenen Verbindungen je nach dem Substitutionstyp und der Natur des aromatischen Kerns unterschiedliche Potentialwerte.

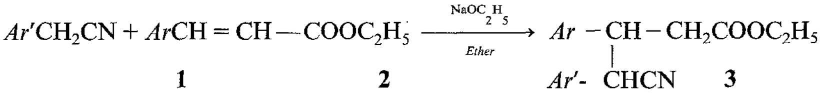
In recent publications [1, 2], we reported the partial contribution of the substituents on the overall anodic oxidation potentials of substituted pyrroles [1], and quinoxalines [2]. More recently, this work has been extended to a series of dipyrrylmethanes, and dipyrrylketones [3]. These studies concluded that the anodic oxidation potentials are correlated to the *pKa* values of arylcarboxylic acids and to the π-electron density of aromatic nucleus. Other workers [4] showed that the polarographic oxidation potentials of aromatic compounds are related to their ionization potentials (energies of HOMO) and to absorption spectra. Anodic oxidation of *p*-disubstituted benzene [5] and other aromatic compounds [6] is reported to give products derived from the initial oxidation of the aromatic species followed by subsequent attack by nucleophiles such as

CN^-, OH^-, CH_3O^-, and AcO^-, in a homogeneous or heterogeneous manner. These electrochemical methods proved to be selective in a fashion that could not be obtained by other methods [7].

To extend the study of organic electrochemistry to other classes of organic compounds, in terms of electrophoric structure-electroactivity relationship, we wish to report here the anodic oxidation potentials of a series of ethyl-3,4-diaryl-4-cyanobutyrates (**3 a–o**), as measured by cyclic voltammetry.

Results and Discussion

We recently synthesized [8] a series of aromatic compounds that comprise cyano and ester groups which might have herbicidal activity. The synthesis was accomplished by *Michael* addition of arylacetonitriles (1) to ethyl cinnamates (2) in the presence of sodium ethoxide suspension in dry ether.



$$\underset{\mathbf{1}}{Ar'CH_2CN} + \underset{\mathbf{2}}{ArCH=CH-COOC_2H_5} \xrightarrow[Ether]{NaOC_2H_5} \underset{Ar'-\,CHCN}{Ar-CH-CH_2COOC_2H_5} \quad \mathbf{3}$$

The products (**3 a–o**) were isolated and identified by standard spectroscopic techniques. Structures are given in Table 1. Cyclic voltammetry measurements were performed on 5 m*M* cyanoesters solution in chromatographic grade acetonitrile, containing 0.1 *M* tetrabutylammonium hexafluorophosphate (*TBAH*) as the supporting electrolyte. These solutions were introduced in a three electrode compartment cell containing a platinum spiral as a counter electrode. The sa-

Table 1. E_p *for compounds* **3 a–o**

3	*Ar*	*Ar'*	E_p, $V_{(vs\,SCE)}$
a	4-Tolyl	4-Chlorophenyl	2.40, 2.70
b	4-Tolyl	2-Fluorophenyl	2.40, 2.70
c	4-Tolyl	4-Bromophenyl	2.40, 2.80
d	4-Chlorophenyl	1-Naphthyl	1.96, 2.80
e	4-Bromophenyl	1-Naphthyl	1.96, 2.80
f	Phenyl	1-Naphthyl	1.96, 2.70
g	2,4-Dichlorophenyl	1-Naphthyl	1.96
h	Phenyl	4-Chlorophenyl	2.70
i	Phenyl	4-Bromophenyl	2.70
j	4-Chlorophenyl	Phenyl	2.70
k	4-Bromophenyl	Phenyl	2.70
l	Phenyl	Phenyl	2.70
m	4-Chlorophenyl	4-Bromophenyl	2.70
n	2,4-Dichlorophenyl	4-Chlorophenyl	2.80
o	2,4-Dichlorophenyl	4-Bromophenyl	2.80

turated calomel electrode was employed as a reference electrode. Cyclic voltammograms were recorded using a combination of a Sycopel Scientific wave form generator type 01, a Hi-Tek potentiostat type DT 2101 and EG and G Princeton Applied Research X-Y recorder model RE 0089. Zero grade nitrogen was bubbled through the solutions for 10 minutes prior to each run, and a sweep rate of 0.1 V/s was used.

The resulting cyclovoltammograms showed well defined current-potential (*i-E*) waves that indicate irreversible electrochemical oxidation at the potential values given in Table 1. Further proof of this irreversibility is evidenced by the higher E_p values obtained at a higher scanning rate. In addition, a slower scanning rate failed to achieve electrochemical equilibrium at the electrode surface so that a reversible wave could not be obtained. Furthermore, the electrochemical oxidation products showed a less active behaviour so that the same voltammogram is reproduced upon repeating the cycle many times.

The anodic oxidation of the cyanoesters (**3a–f**) exhibited two oxidation waves while the compounds (**3g–o**) showed a single oxidation wave, at the E_p-values recorded in Table 1. In these compounds, the aromatic nuclei are most susceptible towards a single electron abstraction. The E_p-values observed for these compounds reflect a straightforward substituent effect. Compounds comprising *Ar′* of 1-naphthyl (**3d–3g**) show an oxidation potential value of 1.96 volts (vs. SCE). This is about 0.74 V lower than that of the phenyl derivative as *Ar* or *Ar′* (compounds **3h–l** showed E_p-value of 2.70 V). These oxidation potential values are comparable to those reported by *Osa* [9] for benzene and by *Weinberg* [10] for naphthalene. The cyanoesters (**3a–c**) containing a 4-tolyl as *Ar* group show an oxidation wave at 2.40 V. This is 0.30 V lower than the oxidation potential of the phenyl derivative. Such an effect is expected to result from the increased π-electron density by the methyl group substituent. On the other hand, compounds containing a halophenyl as *Ar* or *Ar′*, where the halogen atom is Cl, Br or F, show an oxidation potential of 2.70–2.80 V which is not much different from that of phenyl group containing compounds.

In addition, the cyclic voltammograms of all compounds showed that the anodic oxidation process is followed by a cathodic reduction wave at a potential of zero volts. This is comparable to that of proton reduction (*p*-tolounesulfonic acid) in the same medium, as reported [11] for the H^+/H_2 process. This indicates that one electron is abstracted from the π-system of the aromatic species followed by loss of proton to give a short lived aryl radical. The latter then dimerizes and results in the formation of intermolecular electrochemical aromatic coupling product. Such a phenomenon has been repeatedly observed in the literature [12—17] during the anodic oxidation of various aromatic system. The final proof of this assumption must wait until our separation of the oxidation products is complete. Further investigation of this phenomenon is in progress.

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References

[1] *Tabba' HD, Smith KM* (1984) J Org Chem 49: 1870
[2] *Barqawi KR, Atfeh MA* (1987) Electrochemica Acta, in the press
[3] *Tabba' HD, Barqawi KR* (1986) Electrochemica Acta, submitted
[4] *Pysh ES, Yang NC* (1963) J Am Chem Soc 85: 2124
[5] *Rozhkov IN, Alyev IY* (1975) Tetrahedron 31: 977
[6] *Eberson L* (1973) In: *Baizer M* (ed) Organic electrochemistry. M Dekker, New York, pp 447–468, 781–804
[7] *Bloom H, Gutmann F* (1977) Electrochemistry. Plenum, New York, pp 260, and references cited therein
[8] *Al-Arab MM, Issa AM* (1986) J Chem Eng Data 31: 261
[9] *Osa T, Tildiz A, Kuwana T* (1969) J Am Chem Soc 91: 3994
[10] *Weinberg NL, Weinberg HR* (1968) Chem Rev 68: 449
[11] For typical electrochemical behaviour of H^+/H_2 couple, see *Gilman S* (1967) In: *Bard AJ* (ed) Electrochemistry, vol 2. M Dekker, New York
[12] *Nyberg K* (1970) Acta Chem Scand 24: 1609
[13] *Nyberg K* (1971) Acta Chem Scand 25: 534
[14] *Ronlan A, Beckgaard K, Parker VD* (1973) Acta Chem Scand 27: 2375
[15] *Nyberg K* (1971) Acta Chem Scand 25: 2499
[16] *Nilson A* (1978) J Chem Soc Perkin Trans 1: 696
[17] *Beckgaard K* (1972) Tetrahedron Lett 22: 2271