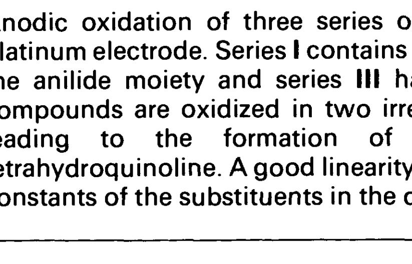
Anodic Oxidation of some Substituted Benzoylacetanilides in Non-aqueous Media

Gouda M. Abou-Elenien,* Bahgat E. El-Anadouli and Ragaii M. Baraka
Department of Chemistry, Faculty of Science, University of Cairo, Giza, Egypt

Anodic oxidation of three series of benzoylacetanilides has been investigated in benzonitrile at a platinum electrode. Series **I** contains substituents on the benzoyl moiety, series **II** has the substituents on the anilide moiety and series **III** has substituents on both benzoyl and anilide moieties. All these compounds are oxidized in two irreversible one-electron processes following the ECEC mechanism leading to the formation of the corresponding substituted 2,4-dioxo-1-phenyl-1,2,3,4-tetrahydroquinoline. A good linearity is obtained when the $E_{\frac{1}{2}}$ values are plotted against the σ substituent constants of the substituents in the different series (**I**—**III**).

The polarographic reduction of a large number of benzoylacetanilides in aqueous media has attracted attention.[1,2] The anodic behaviour of α-cyano-α-ethoxycarbonylthioacetanilides in acetonitrile was studied.[3] To our knowledge no data can be found in the literature on the anodic oxidation of benzoylacetanilides. In the present work, we wish to report the results of anodic oxidation of three series of aroylacetanilides. One series (I) contains substituents on the benzoyl moiety (X), the second (II) has substituents on the anilide moiety (Y) and the third (III) has substituents in both the benzoyl and anilide moieties (X and Y). These compounds are important in the colour photographic process.[4] The measurements were carried out in benzonitrile and acetonitrile with 0.1 mol dm^{-3} $LiClO_4$ as supporting electrolyte at a rotating platinum electrode.



Experimental

Organic Synthesis.—All aroylacetanilides studied were synthesized by the method described in the literature.[5,6] The compounds were recrystallized from EtOH until constant melting points were obtained and were then dried *in vacuo*.

Reagents.—Benzonitrile (BN) and acetonitrile (AN) were purified by classical methods,[7,8] together with the supporting electrolytes $(C_4H_9)_4N^+ClO_4^-$ (TBAP) and $LiClO_4$ which were purified by consecutive recrystallizations and dried before use.

Apparatus and Instruments.—*Voltammetry.* Voltammetric measurements were carried out with a potentiostat-type PCA with its potential source (scan generator VSG 72) (Bank-Electronic, Gottingen, W. Germany) together with an X-Y recorder type servoger XY (Metawatt Nurnberg, W. Germany). A digital Multimeter was used to check the applied potential (type T 2201, Hartman and Braun, W. Germany). The working electrode was a rotating platinum disc of 1.26 mm diameter (type 6.1204 Metrohm Swiss) which was mounted on a motor of the type 628-10 (750 r/m) (Metrohm Swiss).

The electrode potential is expressed *versus* saturated Ag/AgCl/Cl$^-$ (BN) electrode, which was from time to time calibrated against the redox potential of cobaltocinium/cobaltocene system.[9] The standard potential of Ag/AgCl/Cl$^-$ (BN) electrode against the normal hydrogen electrode (NHE) is -176 mV.[10]

Coulometry. The number of electrons transferred in the electrode processes were computed electronically with a coulometer type SS170 in conjunction with the potentioscan VSG 72 (Bank electronic, Gottingen, W. Germany). The IR spectra (KBr disc) were recorded on a Pye Unicam SP-1100 Spectrophotometer, ^{1}H NMR spectra were measured in $CDCl_3$ on a Varian EM-360 90 MHz Spectrometer and chemical shifts are expressed in ppm. Elemental analyses were performed by the Microanalytical Centre, Cairo University.

Controlled Potential Oxidation (*CPO*).—Unsubstituted benzoylacetalide (350 g) in CH_3CN (100 cm^3) containing 0.1 mol dm^{-3} $LiClO_4$ was electrolysed at $+1.8$ V *vs.* Ag/AgCl/Cl$^-$ on a cylindrical Pt gauze anode (*ca.* 80 cm^2). The progress of electrolysis was checked by periodic recording on DC-curves. From time to time the anode was removed from the cell, sprayed with pure acetone and burned in direct flame, cooled and replaced in the cell. The maximum recorded current was 2.6 mA which dropped to 0.3 mA after the loss of two electrons per molecule. At this stage the electrolysis was stopped and the cell was disconnected from the circuit. The mixture was removed and evaporated *in vacuo*. The remaining residue was treated with $CHCl_3$, washed several times and filtered off to remove $LiClO_4$). The filtrate was in turn evaporated *in vacuo*. The remaining product was then crystallized from alcohol. The obtained substance in 75% yield was identified as 2,4-dioxo-1-phenyl-1,2,3,4-tetrahydroquinoline (Found: C, 71.5; H, 4.3; N, 11.0%. Calc. for $C_{15}H_{11}NO_2$: C, 71.71; H. 4.38; N, 11.15%) ν/cm^{-1} (KBr) 3060 (CH aromatic), 2950 (CH, aliphatic), 1720 (C=O, ketonic), 1690 (C=O, amidic). $\delta_H(CDCl_3)$ 4.5 (s, 2 H, $-CH_2-$), 7.2–8 (m, 9 H, aromatic).

On the other hand it is important to mention that CPO experiments in benzonitrile showed several experimental problems, *e.g.* it was very difficult to identify or separate any electrolysis product since the controlled potential value was very high and affected benzonitrile itself. For this reason in large scale preparative electrolysis we used acetonitrile containing $LiClO_4$ and the working electrode was a platinum gauze. Due to the high absorbability of the investigated compounds on the electrode surface, which blocked the electrode and caused high resistance and a simultaneous decrease in current efficiency, the electrode was removed from the cell periodically and cleaned by washing with acetone and burning in a flame.

Results and Discussion

The anodic oxidation of the investigated series of compounds at a platinum electrode in benzonitrile containing 0.1 mol dm^{-3}

Table 1 DC-Voltammetric data of benzoylacetanilides in benzonitrile at rotating platinum electrode

			O$_1$				O$_2$				
X	Y	M.p./°C	$E_{\frac{1}{2}}$/mV	i_L/µA	$E_{\frac{3}{4}} - E_{\frac{1}{4}}$/mV	S^a	$E_{\frac{1}{2}}$/mV	i_L/µA	$E_{\frac{3}{4}} - E_{\frac{1}{4}}$/mV	S^a	σ
Series **I**											
p-NO$_2$	H	161	1180	183	140	135	1750	193	175	135	+0.778
m-Cl	H	127	1130	170	145	118	1680	166	170	128	+0.373
m-OCH$_3$	H	95	1150	208	134	124	1635	215	159	136	+0.115
H	H	106	1120	195	139	136	1600	200	162	148	0.000
m-CH$_3$	H	95	1150	180	148	140	1590	193	158	132	−0.069
p-C$_2$H$_5$	H	97	1130	176	152	139	1580	190	174	154	−0.151
p-CH$_3$	H	112	1150	170	155	130	1580	180	185	162	−0.170
p-OCH$_3$	H	121	1120	203	172	125	1540	196	180	158	−0.268
Series **II**											
H	*p*-NO$_2$	180	1213	215	120	134	1625	220	136	130	+0.778
H	*m*-NO$_2$	137	1195	195	150	128	1620	190	153	134	+0.710
H	*p*-Br	173	1170	197	145	131	1610	203	148	137	+0.232
H	*p*-Cl	156	1190	186	170	125	1615	197	150	144	+0.227
H	*m*-CH$_3$	101	1125	212	175	138	1570	215	165	170	−0.069
H	*p*-CH$_3$	132	1120	180	165	125	1565	190	183	162	−0.170
H	*p*-OCH$_3$	129	1100	175	155	146	1570	182	190	166	−0.268
Series **III**											
p-Cl	*p*-NO$_2$	169	1220	218	148	118	1680	207	163	132	
p-CH$_3$	*p*-NO$_2$	173	1200	195	152	112	1600	199	168	140	
p-NO$_2$	*p*-Br	182	1160	203	138	126	1730	195	170	155	
p-OCH$_3$	*p*-Br	168	1130	208	144	138	1510	200	169	128	
p-NO$_2$	*p*-CH$_3$	156	1130	180	153	150	1700	185	138	136	
p-Cl	*p*-CH$_3$	151	1090	190	163	141	1610	185	128	160	
p-OCH$_3$	*p*-CH$_3$	133	1070	192	129	133	1500	195	166	155	

^{a} $S = dE/d \log (i_d - i)/i$.

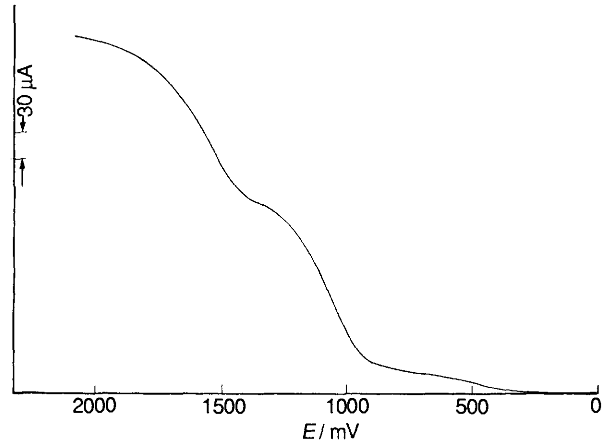


Fig. 1 DC-Voltammogram of unsubstituted benzoylacetanilide in BN at Pt electrode

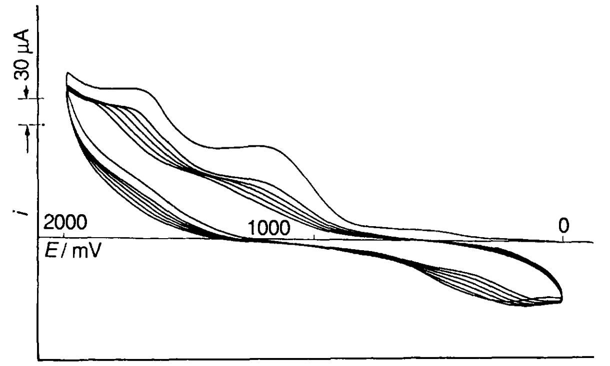


Fig. 2 Oxidation cyclic voltammogram of unsubstituted benzoylacetanilide in BN at Pt electrode

tetrabutylammonium perchlorate as supporting electrolyte was extensively studied. DC-Voltammetric data are compiled in Table 1. Fig. 1 illustrates a typical representative DC-voltammogram while Fig. 2 shows the corresponding cyclic voltammogram. The coulometric measurements indicate that two electrons participate in the whole oxidation process. As shown from the data in Table 1 these compounds are oxidized in two irreversible one-electron waves. The irreversibility of the electrode process is clearly observed from the shape of the cyclic voltammogram.[11] For further confirmation of the irreversibility, logarithmic analysis[12] and $E_{\frac{3}{4}} - E_{\frac{1}{4}}$ relations[13] have been undertaken. The obtained values given in Table 1 indicate that the process is completely irreversible.

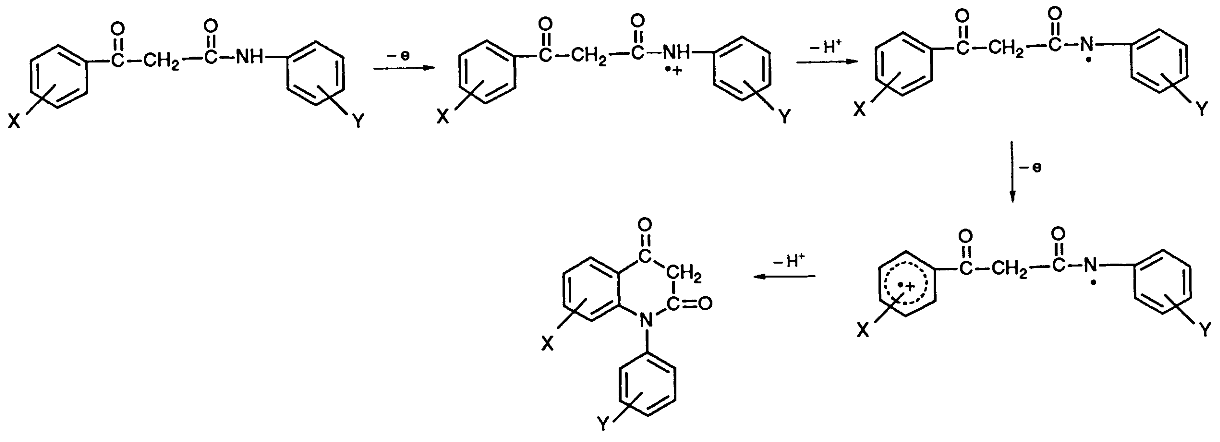
From the obtained data, and isolation and identification of the electrolysis product, Scheme 1 has been suggested as representing the oxidation mechanism.

The electrooxidation process follows the ECEC[14] pattern as illustrated in Scheme 1. The appearance of a small peak in the reverse cycle at a very low positive potential (Fig. 2) is characteristic of the reduction of protons which are lost during the oxidation process. This peak vanishes in light with the addition of solid sodium carbonate.[15]

The effect of substituents on the oxidation of the investigated compounds can be illustrated by applying the modified Hammett equation (1),[16] where σ_x is the Hammett constant,

$$E_{\frac{1}{2}}^{X} = \rho_\pi \sigma_X + E_{\frac{1}{2}}^{H} \qquad (1)$$

ρ_π is the polarographic constant and $E_{\frac{1}{2}}^{X}$ and $E_{\frac{1}{2}}^{H}$ are the half-wave potentials of the substituted and unsubstituted compounds, respectively. Fig. 3 illustrates the Hammett correlations



Scheme 1

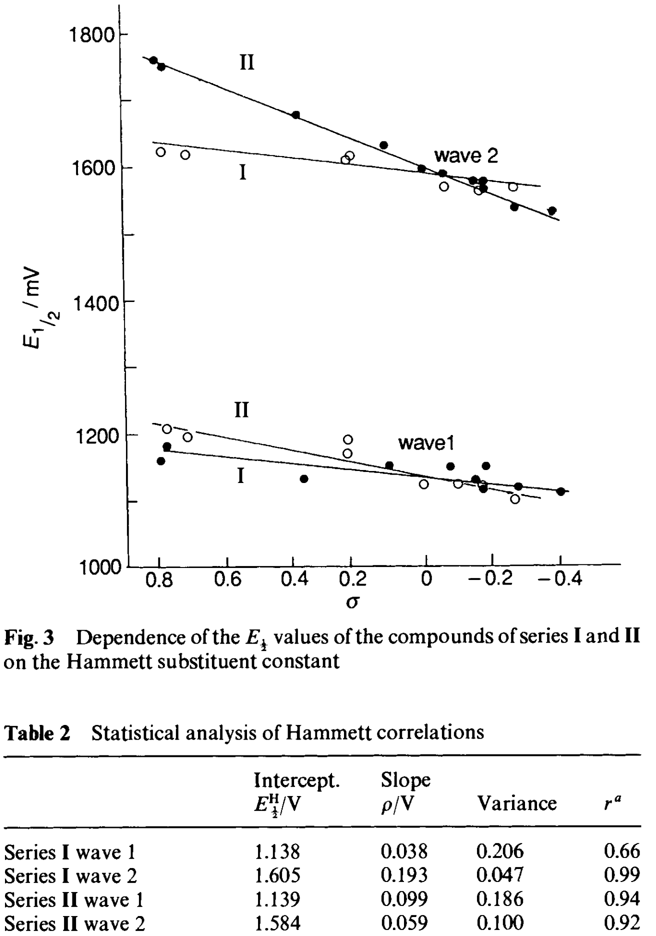


Fig. 3 Dependence of the $E_{\frac{1}{2}}$ values of the compounds of series **I** and **II** on the Hammett substituent constant

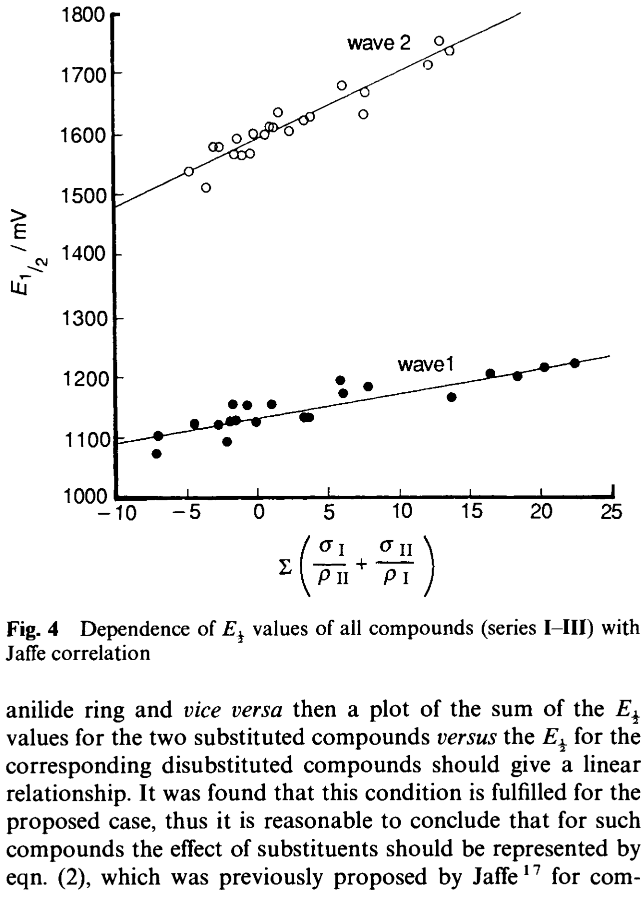


Fig. 4 Dependence of $E_{\frac{1}{2}}$ values of all compounds (series **I–III**) with Jaffe correlation

Table 2 Statistical analysis of Hammett correlations

	Intercept. $E_{\frac{1}{2}}^{H}$/V	Slope ρ/V	Variance	r^a
Series **I** wave 1	1.138	0.038	0.206	0.66
Series **I** wave 2	1.605	0.193	0.047	0.99
Series **II** wave 1	1.139	0.099	0.186	0.94
Series **II** wave 2	1.584	0.059	0.100	0.92
Series **I–III**, wave 1	1.130	0.004	0.314	0.89
Series **I–III**, wave 2	1.590	0.011	0.399	0.91

[a] r = Correlation coefficient.

for the compounds of series **I** and **II**. The statistical analyses of these correlations are compiled in Table 2. As shown from Fig. 3 and Table 2 the substituent (X) in the phenyl ring of the benzoyl moiety (series **I**) has a limited effect on the first oxidation wave and a pronounced one on the second wave. In contrast, the substituent (Y) in the phenyl ring of the anilide moiety (series **II**) has an opposite effect; *i.e.* a pronounced effect on the first wave and a very limited one on the second wave.

In an attempt to gain further information as to the dependence of the electrode process on the nature of the substituent, a series of disubstituted benzoylacetanilidies (series **III**) were studied. If the aroyl substituent (X) has an effect on the electroactive site, independent of the substituent (Y) on the anilide ring and *vice versa* then a plot of the sum of the $E_{\frac{1}{2}}$ values for the two substituted compounds *versus* the $E_{\frac{1}{2}}$ for the corresponding disubstituted compounds should give a linear relationship. It was found that this condition is fulfilled for the proposed case, thus it is reasonable to conclude that for such compounds the effect of substituents should be represented by eqn. (2), which was previously proposed by Jaffe[17] for com-

$$E_{\frac{1}{2}}^{III} = E_{\frac{1}{2}}^{H} + \rho_{I}\sigma_{II} + \rho_{II}\sigma_{I} \qquad (2)$$

pounds containing two substituted benzene rings that are not symmetrically placed with respect to the reaction site. $E_{\frac{1}{2}}^{III}$ is the half-wave potential of compounds of series **III**, σ_I and σ_{II} are the substituent constants for the members of series **I** and **II** respectively, and ρ_I and ρ_{II} are the slopes of correlations between $E_{\frac{1}{2}}^{I}$ and σ_I, and $E_{\frac{1}{2}}^{II}$ and σ_{II}, respectively. To test the validity of such an equation, its linear form was employed [eqn. (3) where $E_{\frac{1}{2}}$ is the half-wave potential of substituted

$$E_{\frac{1}{2}} = E_{\frac{1}{2}}^{H} + \rho_{I}\rho_{II}\left(\frac{\sigma_{I}}{\rho_{II}} + \frac{\sigma_{II}}{\rho_{I}}\right) \qquad (3)$$

derivatives]. In Fig. 4 are plotted the half-wave potentials of 22 compounds studied (series **I–III**) as ordinate and the quantity

$[(\sigma_I/\rho_{II}) + (\sigma_{II}/\rho_I)]$ as abscissa. Clearly all mono- and di-substituted anilides follow this Hammett relationship. These results support the proposed mechanism of oxidation *i.e.* the first oxidation wave corresponds to the oxidation of the (NH) function, and the second to oxidation of the phenyl ring of the benzoyl moiety. Furthermore, the effect of substituent X on the half-wave potential of the second wave is more pronounced than that of substituent Y on that of the first wave. This is because the substituents X are present on the electroactive site *i.e.* phenyl moiety, whereas the substituents Y are present in the phenyl ring attached to the electroactive centre (–CO–NH–).

On the other hand, the substituent in the phenyl ring would be expected to affect the electron density on the electroactive centre. Electron withdrawing groups *e.g.* NO_2 or Cl, lower the electron density and hence make the oxidation more difficult, while the methoxy or methyl groups with their donating power have an opposite effect. As shown from Table 1 and Fig. 3, the results obtained are in full agreement.

References

1 A. S. Shawali and B. E. El-Anadouli, *Can. J. Chem.*, 1976, **54**, 1205.
2 A. S. Shawali, B. E. El-Anadouli and H. M. Sammour, *Electrochim. Acta*, 1976, **21**, 831.
3 D. Berube, G. Cauquis, G. Pierre and H. M. Fahmy, *Electrochim. Acta*, 1982, **27**, 281.
4 C. E. K. Mees, *The Theory of Photographic Processes*, Macmillan New York, 1969.
5 C. J. Kibler and A. Weissberger, *Organic Synthesis*, Coll. vol. 3, 1955, 108.
6 A. S. Shawali, M. M. Naoum and S. A. Ibrahim, *Bull. Chem. Soc. Jpn.*, 1972, **45**, 2504.
7 G. Abou-Elenien, N. Ismail, J. Rieser and K. Wallenfels, *Liebigs Ann. Chem.*, 1981, 1598.
8 W. Summermann, Ph.D. Thesis, Freiburg, Germany, 1970, p. 10.
9 H. M. Koepp, H. Wendt and H. Strehlow, *Z. Elektrochem*, 1960, **64**, 483.
10 G. Wilkinson, *J. Am. Chem. Soc.*, 1952, **74**, 6148.
11 J. Heinze, *Angew. Chem.*, 1984, **23**, 831.
12 J. Tomes, *Collect. Czech. Chem. Commun.*, 1935, **7**, 198.
13 J. Heyrovsky and J. Kuta, *Principles of Polarography*, Publishing House of the Czechoslovak Academy, 1965, p. 129.
14 A. J. Fry, *Synthetic Organic Electrochemistry*, Hayers Row, New York, 1972, p. 88.
15 G. Cauquis, H. M. Fahmy, G. Pierre and M. H. Elnagdi, *Electrochim. Acta*, 1979, **24**, 391.
16 P. Zuman, *Substituent Effects in Organic Polarography*, Plenum Press, New York, 1967.
17 H. H. Jaffe, *Chem. Rev.*, 1953, **53**, 191.

Paper 0/05734G
Received 20*th December* 1990
Accepted 16*th April* 1991