CROATICA CHEMICA ACTA CCACAA **56** (1) 117—123 (1983)

YU ISSN 0011-1643
CCA-1361 UDC 543.253
Original Scientific Paper

Polarographic Investigations of Some 2-Arylazo-2-bromo-5,5-dimethylcyclohexane-1,3-diones

Rajeev Jain

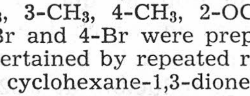
School of Studies in Chemistry, Jiwaji University
Gwaliar, 474011 India

Received December 12, 1982

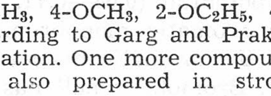
Polarographic reduction of 2-arylazo-2-bromo-5,5-dimethylcyclohexane-1,3-diones takes place in a single step involving two electrons. Well-defined, diffusion controlled, irreversible waves are obtained in the pH range 2.0 — 11.0. The $E_{1/2}$ value shifts towards more negative potentials with increasing pH. Methyl, Methoxy, chloro, bromo and ethoxy groups show positive polarographic ortho shift (Δo). The effect of substituents has been interpreted in terms of the Hammett equation.

Monoarylhydrazones of diketones are important starting materials for the synthesis of compounds of biological importance[1-3]. They are also well known as powerful chelating agents[4]. It has been found that the presence of bromine in the compounds makes them effective antifungal and antibacterial agents[5,6].

A survey of the literature reveals that the redox behaviour of these compounds has not been critically examined. The present paper summarises the results of my studies on the polarographic reduction of 2-arylazo-2-bromo-5, 5-dimethylcyclohexane-1,3-diones (**A**).



(A)



(B)

EXPERIMENTAL

2-Arylazo-2-bromo-5,5-dimethylcyclohexane-1,3-diones (**A**) having substituents, viz., H, 2-CH_3, 3-CH_3, 4-CH_3, 2-OCH_3, 3-OCH_3, 4-OCH_3, 2-OC_2H_5, 4-OC_2H_5, 2-Cl, 3-Cl, 4-Cl, 2-Br and 4-Br were prepared according to Garg and Prakash[7] and their purity was ascertained by repeated recrystallisation. One more compound, 2-Arylazo-5,5-dimethyl cyclohexane-1,3-dione(B) was also prepared in strongly alkaline medium by the literature method[7].

Britton-Robinson buffers in the pH range 2.0—11.0 were prepared by adding suitable amounts of 0.2 M NaOH solution to a stock B. R. buffer solution (pH 1.8) composed of a mixture of boric acid, phosphoric acid and glacial acetic acid. Stock solutions (1.0×10^{-3} M) of 2-arylazo-2-bromo-5,5-dimethylcyclohexane-1,3-diones and 2-arylazo-5,5-dimethylcyclohexane-1,3-dione were prepared in methanol. Solutions of 1.0 M KCl and 1% gelatin were prepared in doubly distilled water. All chemicals used were of A.R. grade.

Apparatus

Polarograms were recorded at $25 + 0.1$ °C with a Cambridge pan recording polarograph. The capillary characteristic was 1.215 $mg^{2/3}$ $S^{1/2}$. A saturated calomel electrode was used as a reference electrode. The pH of the buffer solution was checked by a pH meter ELICO LI-10, using a glass electrode. The millicoulometric method of Devries and Kroon[8] using a mercury pool cathode was employed for determining the value of *'n'*, the number of electrons involved in the reduction using azobenzene in methanol as a standard. Moreover the value of *'n'* was also determined by controlled potential electrolysis, using the formula[9],

$$n = \frac{io}{2.3\, Co\, Fv\, (\Delta \log i / \Delta t)}$$

where, io is the current at $t = 0$ when C=CO, v is the volume of the solution and $\Delta \log i / \Delta t$ is the slope of the plot of $\log i$ against $\log t$. This estimation provided support for the values obtained by the millicoulometric method. The controlled potential electrolysis was carried out at a potential corresponding to the plateau of the wave. The electrolysis cell was an H-shaped vessel, the cathodic and anodic compartment being separated by a diaphragm of sintered glass G-4. Mercury pool was used as a cathode. After complete electrolysis (on 12 hrs) the catholyte was subjected to product analysis. The UV spectra of the solution during electrolysis were recorded at different time intervals on a UV-VIS Carl-Zeiss recording spectrophotometer. Nejedly's method[10] was used to determine the temperature coefficient.

Procedure

Solutions for recording polarograms were prepared by mixing 2.0 ml of stock solution, 4.5 ml of aqueous buffer solution, 2.0 ml of methanol (which was necessary to prevent precipitation) 1.0 ml KCl (1.0 M) and 0.5 ml of freshly prepared 0.1% aqueous solution of gelatin. Reduction in mixtures containing less than 40% methanol was not possible due to the insolubility of the compounds under investigation. The polarograms were then recorded after passing hydrogen for about 10 min.

RESULTS AND DISCUSSION

All (I—XIV) the 2-arylazo-2-bromo-5,5-dimethylcyclohexane-1,3-diones got reduced in a single, 2 electron reduction wave. The number of electrons involved in the reduction was found to be two as obtained by millicoulometric method and supported by controlled potential electrolysis. The wave height of the wave was also compared at various pH (3—9) with azobenzene, benzophenone (total wave height) and nitrobenzene, and was found to the half of that of nitrobenzene but quite comparable to azobenzene and benzophenone in practically identical conditions.

Keeping in view the feasibilities of the sites of reduction, the wave can be assigned to the reduction of the —N=N-bond. Reduction of the C—Br bond at this potential (0.64—0.71, v) looks improbable due to the fact that various other aromatic monobromo compounds in which the bromo group is attached to the aromatic nucleus have been found to be reducible at very high potential. Bromobenzene[11] has been found reducible at 2.32 V. For confirming that the obtained wave is due to the reduction of the —N=N-bond, a compound 2-Arylazo-5,5-dimetylcyclohexane-1,3-dione (B), which does not have the 2-Bromogroup, but is otherwise structurally similar to (**A**), was polarographed in identical conditions. This compound (**B**) got reduced in a single 2-electron wave at a potential 0.04 V positive to the bromo compound. More -ve potential required for the reduction of compounds (**A**) may be due to the presence of the bulky bromo group which shifts the $E_{1/2}$ towards negative potential. Moreover the wave height (i_d) was also found to be slightly higher for the bromo compound.

Controlled potential electrolysis was also carried out for 12 hrs and the products were analysed for any possible bromide ions in the solution. However, no bromide ion could be detected in the electrolysed solution.

Even after extending the potential range by adding tetraalkyl ammonium salt, no second wave (for the reduction of the C—Br bond) even at very high negative potential (—2.6, v) could be realised.

On the basis of the foregoing evidence the polarographic wave obtained can be safely assigned to the reduction of the —N=N-bond in 2-Arylazo-2--bromo-5,5-dimethylcyclohexane-1,3-diones. The height of the wave was limited by diffussion, as was shown by the linear dependence on/h and concentration. The wave height remained practically constant in the entire pH range 2.0—11.0. Low values of the temperature coefficient (1.0—1.4$^0/_0$ deg^{-1}) further supported the diffusion controlled nature of the waves. The $E_{1/2}$ of the waves were found to be dependent on pH and shifted towards more negative potentials with increasing pH. Values of $E_{1/2}$ together with a d $E_{1/2}$/d pH and diffusion current constant (I) are given in Table I. The shift in $E_{1/2}$ towards negative potential with increasing concentration of the depolariser pointed towards the possible role of adsorption[12]. The irreversible nature of the waves was confirmed by log plots. For checking the reversibility of the process, $E_{\mathrm{d.e.}}$ was plotted against log $i/i_d - i$ and it was found that the value of the slope of the above plots appreciably exceeded 59.2/n mv. Moreover, the numerical value of $E_{3/4} - E_{1/4}$ of the polarographic wave appreciably exceeded 56.4/n mV. These two facts confirmed the irreversible nature of the waves. Furthermore, values of k_f°, h were found to be in the range 7.2 to 9.6 × 10^{-11} cm/sec. (Table I).

TABLE I

Polarographic Characteristics of 2-arylazo-2-bromo-5,5-dimethyl-cyclohexane-1,3-diones at pH 3.00, Conc. = 2.0 × 10^{-4} M

No.	R	$-E_{1/2}$/V	i_d/μA	$\frac{dE_{1/2}/\mathrm{mV}}{\mathrm{dpH\ pH}}$	αn	$\Delta E_{1/2}$	I	p	k_f°, h × 10^{-11} cm/sec.
I	H	0.69	1.60	58	0.74	0.00	6.6	0.72	7.5
II	2-CH_3	0.64	1.75	52	0.78	0.05	7.2	0.68	8.2
III	3-CH_3	0.69	1.77	58	0.78	0.00	7.3	0.76	7.5
IV	4-CH_3	0.71	1.77	58	0.74	0.02	7.3	0.72	7.5
V	2-OCH_3	0.67	1.60	52	0.78	0.02	6.6	6.68	8.5
VI	3-OCH_3	0.69	1.60	48	0.80	0.05	6.6	0.64	8.5
VII	4-OCH_3	0.71	1.65	52	0.78	0.02	6.8	0.68	8.2
VIII	2-OC_2H_5	0.68	1.60	52	0.74	0.01	6.6	0.65	8.5
IX	4-OC_2H_5	0.71	1.75	58	0.74	0.02	7.2	0.72	8.2
X	2-Cl	0.66	1.75	52	0.80	0.03	7.2	0.70	8.2
XI	3-Cl	0.66	1.60	52	0.78	0.04	6.6	0.68	8.5
XII	4-Cl	0.68	1.65	58	0.80	0.01	6.8	0.70	8.5
XIII	2-Br	0.65	1.65	52	0.74	0.04	6.8	0.65	8.5
XIV	4-Br	0.68	1.75	52	0.80	0.01	7.2	0.70	8.2

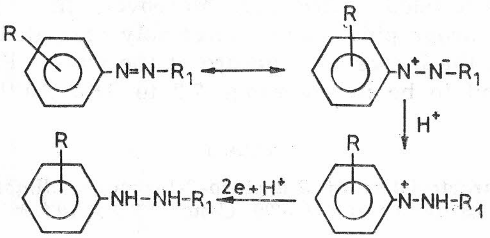
Very low values of K_f°, h clearly indicated the totally irreversible nature of the waves. Hillson and others[13,14] have reported that reduction of azo compounds takes place in a 2-electron wave at the —N=N-group giving the hydrazono derivative provided that an activating group is not present at the -*p* position in the benzene ring. Nygard[15] has reported that reduction of azobenzene gives a reversible 2e wave at low concentration and low pH. The existence of a single irreversible wave observed for these compounds may be attributed to the bulky cyclohexane substituent in the molecule.

The value of αn_a (product of transfer coefficient and number of electrons involved per molecule of the reactant in the rate determining step of the electrode process) and p(number fo protons involved per molecule of the reactant in the rate determining step) were determined using.[12]

$$(E_{1/4} - E_{3/4}) = 0.0517/\alpha n_a$$

$$\frac{d\,E_{1/2}}{\text{dpH}} = \frac{0.5915}{\alpha n_a} \cdot p$$

the values of p are summarised in Table I. The pH dependent nature of $E_{1/2}$ and the independent nature of i_d suggested that both the acidic and basic forms of the compounds reached the electrode surface and are electroactive.[16] It also suggests that the proton transfer step precedes the electrode process. Out of the two possible sequences[16] (H^+, e, H^+, e) or (H^+, 2e, H^+), the latter is more probable.



This mechanism is in accord with the observed pH-dependence of the half-wave potentials as protons are consumed in the reduction process.

The depolariser solution when tested after controlled potential electrolysis, did not give the dye test thereby showing that after reduction of —N=N— to —NH—NH— further reduction to aromatic amine does not take place (As also confirmed by the fact that the number of electrons involved is only 2). The maximum absorbance at 430 nm disappeared in solutions after their complete electrolysis. Further more, the above mentioned electrolysed solution did not give any polarographic wave, thereby confirming the above reduction mechanism.

Effect of Substituents

It is seen from the table that the values of the transfer coefficient αn and $d\,E_{1/2}/d$ pH are reasonably constant for these compounds. The conditions of applying the Hammett equation are thus fulfilled[17]. In order to express the effect of substituents quantitatively the half-wave potential of all these compounds was plotted against the Hammett substiuent constant (values of σ_{o-x}

were from the literature).[18] A linear relationship between the half-wave potential of m- and p-derivatives, viz., 3-CH_3, 4-CH_3, 3-OCH_3, 3-Br, 4-Cl, 4-Br, 3-OC_2H_5 and 4-OC_2H_5 and the Hammett substituent constant (σ) is depicted in Figure 1. (A). It is found that all the derivatives fit in the regression line and the value of the specific reaction constant is 0.10 V. As in this series a sufficient number of half-wave potentials were available for o-derivatives, viz., 2-CH_3, 2-OCH_3, 2-OC_2H_5, 2-Cl and 2-Br, the corrected half-wave potentials for the steric effect for these derivatives were calculated using the following expressions[17].

$$(E_{1/2})\ \text{corrected} = [E_{1/2} - \delta_{\pi,\,R}\,(E_s)_{o-x}]$$

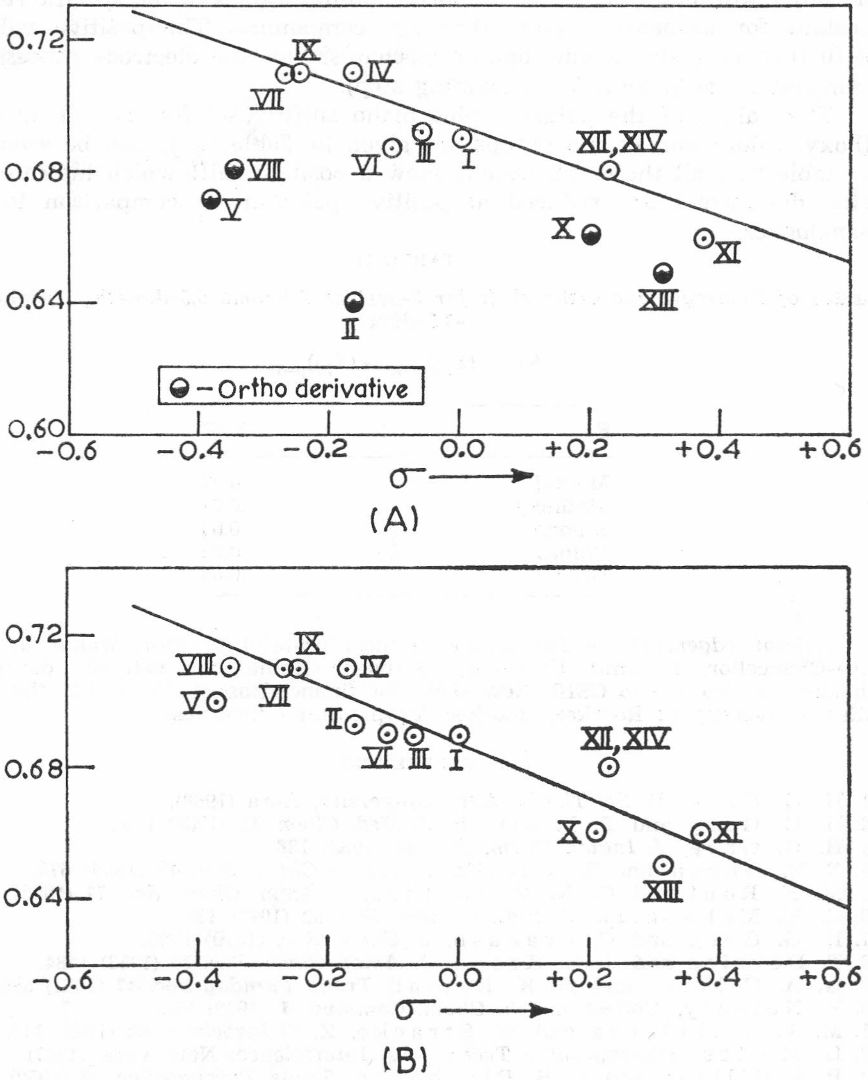


Figure 1. — Plots (*A*)—$E_{1/2}$ vs. and (*B*)—($E_{1/2}$ corrected) vs. σ for 2-arylazo-2-bromo-5,5-dimethylcyclohexane-1,3-diones at pH = 3.0, conc. = 2.0×10^{-4} M.

where

$$\delta_{\pi, R} = \frac{(E_s)_{o-X}}{\Delta E_{1/2} - \delta_{\pi, R}\, \sigma_{o-X}}$$

Values of steric substituent constants $(E_s)_{o-x}$ were taken from the literature (Cf. ref. 17.). The corrected values of half-wave potentials for o-derivatives so obtained were further plotted with *m*- and *p*-derivatives (Figure 1 (B)) and it was found that, with the exception of 3-OCH_3 derivative all the derivatives fit in the regression line. The value of the specific reaction constant (ϱ) for the corrected plot was found to be 0.088 V as against 0.10 V. Florence[19] and other workers[17,18] have also reported similar values of the specific reaction constant for azobenzene and other azo compounds. The positive value of (ϱ) further suggested a nucleophilic mechanism for the electrode process (electron uptake as potential determining step).

The values of the polarographic ortho shift[71] (Δo) for methyl, methoxy, ethoxy, chloro and bromo groups are given in Table II. It can be seen from the table that all these substituent show a positive shift which indicates that ortho derivatives are reduced at positive potential in comparison to their p-analogues.

TABLE II

Values of Polarographic ortho shift for 2-arylazo-2-bromo-5,5-dimethylcyclohexane-1,3-diones

$$\Delta\, o = (E_{1/2})_{o-R} - (E_{1/2})_{p-R}$$

R	Δ_o/V
Methyl	0.07
Methoxy	0.04
Ethoxy	0.03
Chloro	0.02
Bromo	0.03

Acknowledgement. — The author is most grateful to Prof. Wahid U. Malik, Vice-Chancellor, Kashmir University, Srinagar (India) for valuable discussions. Thanks are also due to CSIR, New Delhi for financial assistance and to the authorities, University of Roorkee, Roorkee for providing facilities.

REFERENCES

1. H. G. Garg, *D. Sc. Thesis*, Agra University, Agra (1968).
2. H. G. Garg and P. P. Singh, *J. Med. Chem.* **11** (1968) 1103.
3. H. G. Garg, *J. Indian Chem. Soc.* **40** (1963) 136.
4. N. N. Ghosh and S. Maulik, *J. Indian Chem. Soc.* **46** (1969) 675.
5. M. K. Rout and G. N. Mahapatra, *J. Amer. Chem. Soc.* **77** (1955) 2427.
6. G. N. Mahapatra, *J. Indian Chem. Soc.* **52** (1974) 115.
7. H. G. Garg and C. Prakash, *J. Chem. Soc.* (1970) 1056.
8. T. Devries and J. L. Kroon, *J. Amer. Chem. Soc.* **75** (1953) 1484.
9. G. A. Gilbert and A. K. Rideal, *Trans. Faraday Soc.* **47** (1951) 396.
10. V. Nejedly, *Collect. Czech. Chem. Commun.* **1** (1922) 319.
11. M. V. Stakelberg and W. Stracke, *Z. Elektrochem.* **53** (1949) 118.
12. L. Meites, *Polarographic Techniques, Interscience,* New York (1967).
13. P. J. Hillson and P. B. Birnbourn, *Trans. Faraday Soc.* **48** (1952) 478.
14. I. Tachi, *Mem. Coll. Agr. Kyoto Imp. Univ.*, **17** (1931) 45.
15. B. Nygard, *Ark. Kemi* **26** (1966) 167.

16. P. Zuman, *The elucidation of organic electrode process*, Academic Press, N. Y. (1939).
17. P. Zuman, *Substituent effects in organic polarography*, Plenum Press, N. Y. (1967).
18. H. H. Zaffe, *Chem. Rev.* **53** (1953) 191.
19. T. M. Florence, *J. Electronal. Chem.* **52** (1974) 115.

SAŽETAK

Polarografsko ispitivanje nekih 2-arilazo-2-brom-5,5-dimetilcikloheksan-1,3-diona

Rajeev Jain

Polarografska redukcija 2-arilazo-2-brom-5,5-dimetilcikloheksan-1,3-diona odvija se u jednomu, dvoelektronskom stupnju. U području pH od 2,0 do 11,0 dobije se ireverzibilni, difuzijski kontroliran, dobro definiran polarografski val. Porastom pH poluvalni potencijal se pomiče prema negativnijem potencijalu. Metil-, metoksi-, klor-, brom- i etoksi-skupine uvjetuju pozitivni polarografski orto-pomak. Efekt supstituenata interpretiran je veličinama Hammettove relacije.