# THE POLAROGRAPHY OF THE MONOXIMES AND DIOXIMES OF BENZOQUINONE, NAPHTHOQUINONE, AND ANTHRAQUINONE<sup>1</sup>

### By R. M. Elofson<sup>2</sup> and J. G. Atkinson<sup>3</sup>

#### ABSTRACT

The polarographic behavior of the monoximes and dioximes of 1,4-benzoquinone, 1,4-naphthoquinone, 1,2-naphthoquinone, and 9,10-anthraquinone has been investigated in the pH range 3 to 14. All of the compounds produce welldefined polarographic reduction waves which can be used for analytical purposes. Polarographic evidence indicates that the monoximes and the dioximes exhibit tautomerism.

#### INTRODUCTION

In this investigation the polarography of the monoximes and dioximes of 1,4-benzoquinone, 1,4-naphthoquinone, 1,2-naphthoquinone, and 9,10-anthraquinone over the pH range 3 to 14 has been studied. Because of the structural relationship of the monoximes with nitroso compounds, the polarography of nitrosobenzene has been reinvestigated.

The polarography of 9,10-anthraquinone monoxime (17), 1,4-benzoquinone monoxime (2), and 1,2-naphthoquinone-1-monoxime (8) has been determined previously and separately over different pH ranges. Recently, Souchay and Ser (15), and Calzolari (5) have reported systematic polarographic investigations of the oximes of aromatic ketones. The oxidation-reduction potential of nitrosobenzene has been previously determined by electromotive force measurements by Lutz and Lytton (10) and by polarographic methods by Holleck and Exner (6). No work has been reported on the polarography of the quinone dioximes.

### EXPERIMENTAL

#### A p paratus

A Leeds and Northrup Electrochemograph Type E was used to record the polarograms. A minimum of damping was employed (position 1) to prevent distortion of the waves.

The capillaries that were used were made from marine barometer tubing obtained from the Corning Glass Works. For the data portrayed in Tables I, II, and IV, the value of h was 54.6 cm., t was 4.13 sec., and m was 2.36 mgm./sec. at zero applied voltage vs. saturated calomel electrode in pH 7 buffer and 50% ethanol at 25° C.

The electrolysis cells were of the usual type. A saturated calomel electrode was used as the anode, connected by means of a flexible saturated potassium chloride agar bridge to the electrolysis cell.

<sup>1</sup>Manuscript received August 22, 1955.

Contribution from the Research Council of Alberta, Edmonton, Alberta. <sup>2</sup>Senior Research Chemist, Research Council of Alberta, Edmonton, Alberta.

<sup>3</sup>Laboratory Assistant, Research Council of Alberta, Edmonton, Alberta.

# Media

Buffers were prepared according to Clark and Lubs; pH measurements of alcohol mixtures were recorded with a Beckman Model G pH meter and glass electrode.

## Chemicals

1,4-Benzoquinone monoxime, m.p. 136-138° C. (decomp.), and 1,4-benzoquinone dioxime, m.p. 247-248° C. (decomp.), were prepared according to Beilstein.

9,10-Anthraquinone monoxime, m.p. 222-223° C. (decomp.), was prepared according to Julian (7).

9,10-Anthraquinone dioxime was prepared by treating 5 gm. 9,10-anthraquinone with 10 gm. hydroxylamine hydrochloride in 50 ml. of pyridine; the yield was quantitative. Upon recrystallization from methanol it melted at  $259-260^{\circ}$  C. (decomp.) (11).

1,2-Naphthoquinone-2-monoxime, m.p. 165–167° C. (decomp.), and 1,4-naphthoquinone monoxime, m.p. 190–192° C. (decomp.), were prepared according to Beilstein from  $\alpha$ -naphthol.

1,2-Naphthoquinone dioxime, m.p. 150° C. (decomp.), and 1,4-naphthoquinone dioxime, m.p. 221° C. (decomp.), were prepared from the corresponding monoximes by treatment with hydroxylamine hydrochloride and pyridine in alcohol according to Beilstein.

Nitrosobenzene, m.p. 66.5-68° C., was purified by recrystallization from ether.

### RESULTS

### The Polarography of Nitrosobenzene

In Table I are tabulated the half-wave potentials of nitrosobenzene over the pH range 6 to 11.

TABLE I

	HALF	WAVE POT Conce	TENTIALS OF	NITROSOBEN $ imes 10^{-4}~M$ a	zene vs. S. approx.	C.E.
A.	Water solution pH	6	7	9	10	
	$-E_{\frac{1}{2}}$ volts	0.012	0.075	0.185	0.245	
В.	Alcohol 52% b pH	y volume 6.3	8.3	10.4	11.4	0.1 <i>N</i> NaOH
	$-E_{\frac{1}{2}}$ volts	0.072	0.190	0.320	0.380	0.480

The first series of measurements carried out in aqueous solution obey equation [I]:

$$E_{\frac{1}{2}}$$
 vs. S.C.E. =  $+0.339 - 0.0584$  pH. [I]

This represents the reversible nitrosobenzene-phenylhydroxylamine system whence the normal electrode potential  $E_0$  becomes 0.339+0.246 = 0.585 v.,

 $\mathbf{5}$ 

#### CANADIAN JOURNAL OF CHEMISTRY, VOL. 34, 1956

which is in excellent agreement with the results of Lutz and Lytton (10) who obtained  $E_0$  equal to 0.582 v. by potentiometric titration.

In alcohol solution the relationship between the half-wave potential and the pH as measured with the glass electrode is exactly linear but the equation is given by [II]:

 $E_{\frac{1}{2}}$  vs. S.C.E. = +0.323 - 0.0603 pH, [II]

whence  $E_0$  becomes 0.569 volts. The discrepancy in the results, which amounts to about 50 mv. in the actual measurements, is presumably partly due to the errors of measuring pH with the glass electrode in nonaqueous solutions. Similar considerations would probably apply to the other measurements recorded in this paper.

Because of the high volatility of nitrosobenzene exact diffusion current measurements were not made, but the wave heights indicated quite clearly that two electrons were involved in the reduction. This was also evident from a plot of  $E_{de}$  vs. log  $[i/(i_d-i)]$ . Straight lines were obtained with a slope of 27 mv. at pH 7 and 31 mv. at pH 10, which agree well with the theoretical value of 29 mv. for a two-electron reduction.

# The Polarography of the Quinone Dioximes

The half-wave potentials of the quinone dioximes in alcohol solution are presented in Table II. All the dioximes were reduced in acid solutions and in strongly alkaline solutions by a process involving six electrons. This was established by comparing the wave heights for anthraquinone dioxime and benzophenone in tetramethylammonium hydroxide solution. Under these

TABLE II

Half-wave potentials vs. S.C.E. of Quinone dioximes Concentration 1.67  $\times$  10<sup>-4</sup> M in 55% ethanol (minor waves in brackets)

	Dioximes								
-	1,4-Benzo- quinone		1,4-Naphtho- quinone		1,2-Naphtho- quinone		9,10-Anthra- quinone		
pH	$-E_{\frac{1}{2}}$ , volts	n*	$-E_{\frac{1}{2}}$ , volts	n*	$-E_{\frac{1}{2}}$ , volts	n*	$-E_{\frac{1}{2}}$ , volts	n*	
3.1	0.09	6	0.13	6	0.07	6	0.37	6	
3.9	0.16	6	0.21	6	-	_	0.49	6	
5.3	0.30	_	0.34(0.47)	<b>6</b>	0.30	6	0.61	6	
6.3	0.39(0.52)								
7.3	0.54	_	0.51	6	0.38	6	0.72	6	
8.4	0.80	_	-		0.48	-	0.82	6	
9.4	(0.79)0.96		()0.95	-	0.61()	-	0.86()	-	
10.4	1.10	6	ì.01	_	(0.82)1.02	_	(-)1.27	_	
11.4					1.05	6	1.32	6	
0.1 N NaOH	1.12	6	1.26	6	1.15	6	1.38	6	
0.05 M (CH <sub>3</sub> ) <sub>4</sub> NOH	1.11	6	1.14	6	1.09	6	1.38	6	

\*Number of electrons.

conditions a  $2.7 \times 10^{-4} M$  solution of benzophenone produced a wave of 1.31 µa. and a  $0.9 \times 10^{-4} M$  solution of anthraquinone dioxime produced a

# ELOFSON AND ATKINSON: POLAROGRAPHY

wave of 1.30  $\mu$ a. Since the number of electrons required for the polarographic reduction of benzophenone in alkaline solution is known to be two, it follows that the number of electrons required in the reduction of anthraquinone dioxime must be six. The corresponding value for a  $0.9 \times 10^{-4}$  M solution of benzoquinone dioxime was 1.36  $\mu$ a. under the same conditions. At a pH of 3.1 the diffusion currents of  $0.9 \times 10^{-4}$  M solutions of 1,4-benzoquinone dioxime and 9,10-anthraquinone dioxime in the same concentration of alcohol were respectively 1.32 and 1.26  $\mu$ a. Therefore it follows that the number of electrons required at the low pH is likewise six. The height of the reduction wave of both of the naphthoquinone dioximes likewise corresponded to the assignment of six-electron reduction waves at low and high pH's.

The surprising equality of the diffusion currents for anthraquinone dioxime and benzoquinone dioxime, despite the fact that the molecular weight of the former was much larger than that of the latter, prompted a controlled potential analysis of anthraquinone dioxime. This was carried out with a 0.001 M solution in 50% ethyl alcohol and buffer of pH 4. A stirred mercury pool was used as cathode and a saturated calomel electrode as anode in order to prevent formation of oxygen. After electrolysis for 12 hr. no cathodic current remained on a test polarogram. Instead, an anodic wave was obtained at -0.20 v. The original cathodic current was 20  $\mu$ a. The anodic current was 6.5  $\mu$ a. or almost exactly one-third of the original cathodic wave. Anthrahydroquinone produced an anodic wave under these conditions at about -0.4 v. Since the diamine would have a higher oxidation potential than the anthrahydroquinone, that is, a more positive polarographic oxidation potential, the anodic wave corresponds to the wave of the expected diamine. Further confirmation of this hypothesis resulted when the alcohol was removed under vacuum and a reddish-brown powder was obtained which decomposed at 190° C.; reported m.p. for anthracenediamine 196° C. (14). The powder dissolved in hydrochloric acid and, upon heating, anthraquinone-identified by melting point 270-275° C. with sublimation—was precipitated out (18).

Variation of the height of mercury in the column showed that the height of the reduction waves varied with the square root of h (Table III). This indicates that the waves are diffusion-controlled in both acid and alkaline solutions.

At intermediate pH's the polarograms may show reduction in two steps and the total height of the waves does not correspond to an integral number of electrons. Detailed examination of these waves showed that the lower wave was rate-controlled, while the upper wave was diffusion-controlled, at least when it was the dominant wave. This was proved by the fact that the height of the lower wave was independent of the height of mercury in the reservoir while the height of the upper wave varied with the square root of the height of mercury in the reservoir as shown in Table III.

Kolthoff and Liberti (9) observed similar behavior in the polarographic reduction of N-nitrosophenylhydroxylamine. These authors attributed the kinetic current to the fact that the lower wave corresponded to the reduction of the neutral molecule and the higher wave to reduction of the anion. How-

# CANADIAN JOURNAL OF CHEMISTRY. VOL. 34, 1956 TABLE III

Diovima	рН		Curre	Ratio*	
Dioxime		_	$h_2 = 55.6$ cm.	$h_1 = 35.6 \text{ cm.}$	at $h_2/h_1$
9,10-Anthraquinone	3.1		1.54	1.26	1.22
1,4-Benzoquinone	3.1		1.68	1.32	1.27
1,4-Benzoquinone	10.4	Upper	1.32	1.06	1.25
		Lower	0.38	0.38	1.00
9,10-Anthraquinone	10.4	Upper	1.36	1.12	1.21
		Lower	0.25	0.25	1.00
1,4-Benzoquinone	7.3		0.62	0.62	1.00

Effect of mercury heights on reduction waves of quinone dioximes Concentration  $0.9\times10^{-4}~M$  in 50% ethanol

 $\sqrt[*]{(h_2/h_1)} = 1.25.$ 

8

ever, at the intermediate pH's the concentration of the neutral molecule was calculated to be much smaller than that which corresponded with the height of the reduction wave attributed to it. The height of this wave then corresponded with the rate of formation of the neutral molecule from the anion. Similar behavior has been observed with pyruvic acid and has been attributed by Brdicka (4) to slow formation of the undissociated acid from the anion at the electrode.

However, while the behavior of the quinone dioximes resembles that of these compounds, the kinetic waves cannot arise from the same reason since the dissociation constants are much smaller ( $k = 10^{-10}$  to  $10^{-12}$ ) than for the compounds just discussed. This fact suggests that isomerization takes place at the electrode at intermediate pH's before reduction occurs. This will be discussed more fully in a subsequent section.

The diffusion currents vary directly with concentration in both acid and alkaline solutions over the concentration range studied of about 0.9 to  $1.67 \times 10^{-4} M$ . At intermediate pH's the waves may be indefinite enough to make quantitative measurement difficult.

The variation of the half-wave potentials with concentration has not been studied in detail. In acid solutions the half-wave potential of anthraquinone dioxime varies markedly with concentration. Changing the concentration from  $0.9 \times 10^{-4} M$  to  $1.67 \times 10^{-4} M$  changes the half-wave potential 0.22 v, whereas with benzoquinone dioxime the variation is muchless than 0.01 v. for a similar change. In alkaline solutions the half-wave potentials are independent of concentration.

## The Polarography of the Quinone Monoximes

The half-wave potentials of the quinone monoximes at various pH values in 55% ethanol are presented in Table IV. Inspection of the table shows that reduction involves four electrons at all pH values for the four compounds, with the exception of 1,4-benzoquinone monoxime at low pH values and 1,4-naphthoquinone monoxime at pH 10.4 and 11.4. In the latter cases the height of the waves is somewhat smaller than that corresponding to fourelectron reductions. Previous workers have reported four-electron reduction for benzoquinone monoxime (2) and anthraquinone monoxime (17).

### ELOFSON AND ATKINSON: POLAROGRAPHY

### TABLE IV

HALF-WAVE POTENTIALS VS. S.C.E. OF QUINONE MONOXIME
Concentration 1.67 $\times$ 10 <sup>-4</sup> M in 55% ethanol
(minor wayes in brackets)

	Monoximes								
	1,4-Benzo- quinone		1,4-Naphtho- quinone		1,2-Naphtho- quinone		9,10-Anthra- quinone		
pН	$-E_{\frac{1}{2}}$ , volts	n*	$-E_{\frac{1}{2}}$ , vol	ts n*	$-E_{\frac{1}{2}}$ , volts	n*	$-E_{\frac{1}{2}}$ , volts	n*	
3.1		_	_	_	0.02	4	0.23	4	
3.9 5.3	$\begin{array}{c} 0.04 \\ 0.14 \end{array}$	_	$0.13 \\ 0.25$	$\frac{4}{4}$	$0.05 \\ 0.16$	$\frac{4}{4}$	$0.29 \\ 0.38$	4 4	
7.3 8.4	$0.24 \\ 0.31$	$^{(4)}_{4}$	$0.31 \\ 0.35$	$\frac{4}{4}$	0.23	4	$\begin{array}{c} 0.48 \\ 0.59 \end{array}$	4 4	
9.4	0.46  0.63	4	0.41	4	0.35	4	0.58	Â	
10.4 11.4	0.88	$\frac{4}{4}$	() 0.56 0.	75 - 81 - 100	0.55	$\frac{-}{4}$	0.63	44	
0.1 N NaOH	0.82	4	0.88	4	0.65 & 0.78	4	0.91	4	

\*Number of electrons.

The fact that four electrons are involved in the reductions was established not only by comparison with the dioximes but by comparison with p-nitrophenol, the polarography of which has been elucidated by Astle and McConnell (2) and by Stocesova (16). In 0.1 N NaOH and 50% ethanol the current due to p-nitrophenol at a concentration of  $0.9 \times 10^{-4} M$  was 1.48  $\mu$ a. and to benzoquinone monoxime at the same concentration was 1.0  $\mu$ a. Since the reduction of p-nitrophenol in alkaline solutions involves six electrons, the reduction of the quinone monoxime involves four electrons.

The reduction of the quinone monoximes proceeds in single steps in acid solutions. In alkaline solutions one wave only is obtained except in the case of the monoxime of 1,2-naphthoquinone in which a stepwise reduction occurs. 9,10-Anthraquinone monoxime provides only one reduction wave at all pH's studied. The other compounds show double waves in the pH range 9 to 11.

TABLE V

8			Curr	Ratio*		
Monoxime	pH		$h_2 = 5.6 \text{ cm}.$	$h_1 = 35.6 \text{ cm}.$	at $h_2/h_1$	
1,4-Benzoquinone	4.3		1.4	1.3	1.07	
1,4-Benzoquinone	9.4	Lower	0.48	0.48	1.00	
		Upper	1.4	1.0	1.4	
9.10-Anthraquinone	3.1		1.68	1.34	1.25	
9,10-Anthraquinone	13.9		1.80	1.36	1.32	

 $\sqrt[*]{(h_2/h_1)} = 1.25.$ 

Since it was observed that only *p*-benzoquinone monoxime showed abnormally small diffusion currents at low pH's, these were investigated further by varying the height of the mercury reservoir as illustrated in Table V. These

9

# CANADIAN JOURNAL OF CHEMISTRY. VOL. 34, 1956

results indicate clearly that the wave at high pH's is diffusion-controlled for both 1,4-benzoquinone monoxime and 9,10-anthraquinone monoxime but only for 9,10-anthraquinone monoxime at low pH's. 1,4-Benzoquinone monoxime at low pH shows a reduction wave which is almost purely kinetic in nature, and this persists to the region where a double wave is observed. This proves that at low pH's the reduction of this compound must be preceded by a change at the surface of the electrode before reduction can take place. Since this reaction could not be the formation of the undissociated acids from the anion (pK for benzoquinone monoxime is about 6), it must involve tautomerization. This may involve the system p-nitrosophenol – benzoquinone monoxime or p-benzoquinone monoxime – p-benzoquinone nitrone.

The diffusion currents have been found to be directly proportional to concentration in the range studied of 0.9 to  $1.67 \times 10^{-4} M$ .

The half-wave potentials were subject to less variation with concentration than was the case with the dioximes. In the case of anthraquinone monoxime at pH 5.3 changing the concentration from  $0.9 \times 10^{-4} M$  to  $1.67 \times 10^{-4} M$ changed the half-wave potential by 0.01 v. In more acid solutions, and also in alkaline solutions, the half-wave potentials were much less dependent or not dependent at all on concentration.

### DISCUSSION

The polarographic reduction of the oximes of aromatic ketones (5, 15) has been shown to involve four electrons and results in the production of the corresponding amine. Since the polarographic reduction of the quinone dioximes requires six electrons, the products of the reduction of these substances must be the corresponding diamines, according to equation [III]:



In the preceding section it has been shown that reduction in neutral solutions is stepwise. Since the lower wave is a kinetic wave, isomerization at the electrode before reduction must be postulated. As it has been pointed out, this must involve tautomerization and not simply re-formation of the undissociated oxime from the anion. Presumably this must involve some form of the classical nitrone-oxime isomerization, equation [IV], postulated originally by Angeli (1) and applied to dioximes by Ponzio (12):

$$C = \text{NOH} \quad \leftrightarrow \quad C = \underset{H}{N \to 0}. \quad [IV]$$

It is not possible from the results of this study to state which form is actually reduced at the electrode, but it is hoped that a consideration of these results

Can. J. Chem. Downloaded from www.nrcresearchpress.com by UNIVERSITY OF NORTH TEXAS LIBRARY on 11/26/14 For personal use only.

with infrared and ultraviolet spectra analyses currently in progress will elucidate this isomerism. In strongly alkaline solutions, the anion is stabilized by resonance and the molecule is reduced at a considerably higher potential.

The actual reduction probably proceeds according to equation [V]:



through the intermediate diimino compound. This mechanism is supported by the fact that the slope of the plot of  $E_{\frac{1}{2}}$  vs. pH in acid solutions approximates 0.100, which corresponds to a critical step involving four H<sup>+</sup> and presumably four electrons. The results of catalytic and electrolytic reduction of various oximes has necessitated the hypothesis of a similar mechanism. These reductions result in the formation of mixtures of both primary and secondary amines. In order to explain this, von Braun (3) postulated similar imino intermediates which condense with the amine already produced. Elimination of ammonia and further hydrogenation results in the formation of the secondary amine according to equation [VI]:

$$\begin{array}{cccc} R_1R_2C = NOH & \xrightarrow{H_2} & R_1R_2C = NH \xrightarrow{H_2} & R_1R_2CHNH_2 & [VI] \\ & & \downarrow & + R_1R_2CHNH_2 \\ & & & \downarrow & + R_1R_2CHNH_2 \\ & & & R_1R_2CH - NH - CHR_1R_2 \xrightarrow{-NH_3} (R_1R_2CH)_2NH. \\ & & & \downarrow \\ & & & NH_2 \end{array}$$

As illustrated in Table III, the polarographic reduction of benzoquinone dioxime at a pH of 7.3 results in a single wave of about one-half the normal height. Since this is a kinetic wave whose height depends on a rate of isomerization, no conclusion can be drawn, at this pH, about the formation of final reduction products corresponding to the dihydroxylamine or the diimino compound. That is, the small wave height may be due entirely to slow isomerization of the dioxime, and only the normal reduction product—the diamine—may be produced.

In all cases where diffusion-controlled waves were observed the reduction of quinone monoximes involves four electrons; hence the over-all reduction product must be the corresponding aminophenol over the entire pH range. On the other hand, the reduction of nitrosobenzene has been shown to stop at the phenylhydroxylamine stage in the pH range studied here. The polarographic reduction of nitrobenzene proceeds to phenylhydroxylamine in alkaline solution, and to aniline in acid solution. *p*-Nitrophenol is reduced stepwise at

### CANADIAN JOURNAL OF CHEMISTRY. VOL. 34, 1956

nearly all pH values to p-aminophenol. In the case of p-nitrophenol these observations have been explained by the hypothesis of quinoidation (16), according to equation [VII]:



However, p-nitrosophenol (benzoquinone monoxime) is reduced in one step and at more positive potentials than p-nitrophenol. For p-nitrophenol, at pH 3, Astle and McConnell (2) report a stepwise reduction at  $E_{\frac{1}{2}} = -0.41$ and -0.86 v. whereas this investigation has shown a single step reduction at pH 3.9 of  $E_{\frac{1}{2}} = 0.04$  v. for benzoquinone monoxime. Furthermore, at pH 12, they found that  $E_{\frac{1}{2}}$  was -0.93 v. and -1.57 v. for p-nitrophenol, whereas at pH 11.4 this investigation showed  $E_{\frac{1}{2}} = -0.88$  v. for benzoquinone monoxime.

These results indicate that the reduction of the monoximes does not involve the intermediate formation of p-hydroxylphenylhydroxylamine which would be expected during the reduction of p-nitrosophenol, but rather the reduction of the oxime according to equation [VIII]:



This mechanism is supported by the results of the reduction of the quinone dioximes and by the results of the chemical reduction of oximes. The fact that the wave for 1,4-benzoquinone monoxime at low pH's is a kinetic wave indicates that the oxime or other species actually reduced must form slowly at the electrode before reduction can take place. The other monoximes either do not need to rearrange before reduction, or else rearrange very rapidly. As discussed in the section on the dioximes, the possibility of the existence of nitrone forms of the oximes must be considered. This point will require further investigation but the ultraviolet work of Ramart-Lucas (13) confirms the existence of three forms of benzoquinone monoxime in buffered solutions. These are probably nitrosophenol, benzoquinone monoxime, and the corresponding nitrone.

Whereas the reductions of the quinone oximes are irreversible and no particular significance should be placed on the slope of the waves, it is interesting to compare the values obtained by plotting  $E_{de}$  vs. log  $[i/(i_d-i)]$ . In alkaline solution no variation of the slope as a function of structure is obtained, but in acid solution the values obtained for the corresponding monoximes at pH 3.9 are: 1,4-benzoquinone 32 mv.; 1,2-naphthoquinone 52 mv.; 1,4-

12

Can. J. Chem. Downloaded from www.nrcresearchpress.com by UNIVERSITY OF NORTH TEXAS LIBRARY on 11/26/14 For personal use only.

### ELOFSON AND ATKINSON: POLAROGRAPHY

naphthoquinone 58 mv.; and 9,10-anthraquinone 73 mv. The corresponding figures for the dioximes at pH 3.1 are 36 mv., 35 mv., 47 mv., and 69 mv., respectively. The values correspond to actual slopes that are much too low for the number of electrons involved in the reduction. However, it is noteworthy that the derivatives of benzoquinone have much steeper waves than the derivatives of anthraquinone. The derivatives of the two naphthoguinones have waves of intermediate slope. This, of course, is the order of aromaticity of the parent hydrocarbons, the oxidation potentials of the corresponding quinones, and, particularly, the order of conjugation between the functional groups in the oximes themselves.

Since the reactions are highly irreversible, it is not feasible to attach much significance to the actual half-wave potentials of the monoximes and dioximes and their relationship to the reduction potentials of the quinones. However, the fact that the half-wave potentials of the anthraquinone derivatives are at the more negative potentials, and those of benzoquinone derivatives are at more positive potentials, indicates that conjugation is the controlling factor. Since 1,2-naphthoquinone derivatives have potentials very close to those of the benzoquinone oximes, this would indicate a very high degree of conjugation due to proximity of the functional groups.

#### REFERENCES

 ANGELI, A., ALESSANDRI, L., and AIAZZI-MANCINI, M. Atti accad. Lincei, 20: 546. 1911.
ASTLE, M. J. and MCCONNELL, W. V. J. Am. Chem. Soc. 65: 35. 1943.
VON BRAUN, J., BESSING, G., and ZOBEL, F. Ber. 56: 1988. 1923.
BRDICKA, R. Listy, 40: 232. 1946.
CALZOLARI, C. Bull. soc. adriat. sci. nat. Trieste, 45: 109. 1949-50. Chem. Abstr. 405.2105. 46:3423. 1952.

6. HOLLECK, L. and EXNER, H. J. Naturwissenschaften, 39: 159. 1952.

JULIAN, P., COLE, W., and DIEMER, C. J. Am. Chem. Soc. 67: 1721. KOLTHOFF, I. M. and LANGER, A. J. Am. Chem. Soc. 62: 3172. 1940 KOLTHOFF, I. M. and LIBERTI, A. J. Am. Chem. Soc. 70: 1885. 1948 1945

1940.

1948

1938

 KOLHOFF, I. M. and LYTTON, M. R. J. Org. Chem. 2:68. 193
MEISENHEIMER, J. and MAHLER, E. Ann. 508: 185. 1934.
PONZIO, L. G. Ber. 61, B: 1316. 1928.
RAMART-LUCAS, P. and MARTYNOFF, M. Bull. soc. chim. F Bull. soc. chim. France, 53. 1949.

14.

15.

16.

17.

SCHIEDT, B. J. prakt. Chem. 157: 203. 1941. SOUCHAY, P. and SER, S. J. chim. phys. 49: C172. 1952. STOCESOVA, D. Collection Czechoslov. Chem. Communs. 14: 615. 1940. STONE, K. G. and FURMAN, N. H. J. Am. Chem. Soc. 70: 3062. 1948. VOROZSHTSOV, N. M. and SHIKITIN, V. P. J. Gen. Chem. (U.S.S.R.), 10: 883. 1940.